COMPLEXATION OF METAL IONS WITH 3,5-DI-*TERT*-BUTYL-1,2-BENZOQUINONE-1-MONOOXIME, ESR STUDIES OF RADICAL INTERMEDIATES

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The possibility of chelate formation of 3,5-di-*tert*-butyl-*o*-benzoquinone-1-monooxime with Cu(II), Co(II), Ni(II), Mn(II), Pd(II) metal ions under N_2 and in air have been investigated. It was found that complexation of metals except Cu(II) and Mn(II) was accompanied by formation of various stable radical species under air. The complexation of Co(II) even under N_2 unlike other metal ions, results in the formation of very stable radical species, which are assigned to phenazinyl type radical. ESR examination of reduction of bis(3,5-di-*tert*-butyl-*o*-benzoquinone-1-monooximato)M(II) (M = Cu, Pd,) with triarylphosphines $P(C_6H_4X)_3$ (X = H, *m*-Cl, *m*-CH₃, *p*-Et₂N) reveal the formation of the N-(2'-hydroxy-3,5-di-tertbutylphenyl)-4',6'-di-tertbutyl-*o*-benzosemiquinone iminate radical. Finally, ESR spectra of Cu(II), Ni(II), and Mn(II) complexes at 300 and 130 K, as well as reaction of bis(oximato)Ni(II) with PPh₃ have been studied.

Keywords: 3,5-di-*tert*-butyl-1,2-benzoquinone-1-monooxime; Optical and ESR spectra; Radical intermediates; Transition metal complexes

INTRODUCTION

Adducts between paramagnetic metal ions and organic radicals can provide specific information on the nature of radical intermediates which are often

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the products of the complexation of metal ions with redox-active ligands [1 – 5]. Electron transfer reactivity of coordination compounds has become an area of extensive research in recent years, and radical ligand complexes have frequently been found as crucial intermediates in catalytic processes, including photo-, electro-catalytic cycles [1, 4, 5]. Quinines and their one- and two-electron reduction products (semiquinones and catechols) play an important role in many biological electron-transfer processes and sometimes function in conjunction with a redox-active metal center [2, 3, 5]. Many of the unique and interesting properties of transition metal complexes containing quinone ligands arise from the similarity in energy between the redox-active quinone electronic levels and the metal orbitals [2, 3, 6, 7]. It has been demonstrated that quinone radicals are involved in single electron transfer in respiration and photosynthesis [3, 5]. Although the coordination chemistry of catechols and quinones has been studied extensively, these compounds constitute an interesting class of bidentate ligands [2 – 7]. At the same time, to our knowledge, the complexation of 3,5-di-*tert*-butyl-*o*-benzoquinone-oxime (QH) which is isoelectroni with DTBQ has not been reported. Another interesting behavior of this oxime, unlike DTBQ, is its capability to exist in polar solvents with both isoelectronic oxime and nitroso tautomer structures, and therefore the formation of complexes containing both tautomers is not ruled out.

In the course of our investigations of transition metal complexes with redox-active ligands containing sterically hindered phenol fragments [8, 9], the present study investigates the complexation ability of QH with M(acetate)$_2$ [where M = Cu(II), Co(II), Ni(II), Pd(II) and Mn(II)], spectroscopic characterization (IR, UV-Visible, ESR) of the prepared compounds, ($MQ_2 \cdot 2H_2O$), and examination of their reactivity towards triphenylphosphine.

EXPERIMENTAL

Elemental analyses were carried out at the Turkish Center Science and Technology Research Council (TÜBITAK) in Gebze. UV-Visible spectra
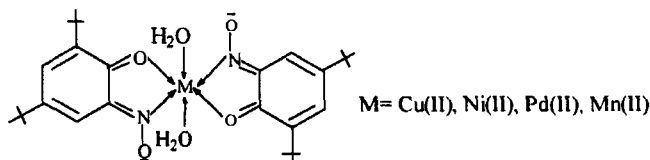

FIGURE 1 The structure proposed for $MQ_2 \cdot 2H_2O$.

were recorded on a Shimadzu UV-160A spectrophotometer. Infrared spectra were obtained on a MATTSON 1000 FTIR spectrophotometer using KBr discs. The magnetic susceptibility measurements were carried out by the Faraday technique with a Sherwood Scientific magnetic susceptibility (Model No: MK1) balance at room temperature using $Hg[Co(NCS)_4]$ as the standard. Diamagnetic corrections for the ligands were calculated using the Pascal constants and temperature independent paramagnetism (60×10^{-6}) [10]. The ESR spectra were recorded on a Varian E-109C spectrometer operating at X-band with 100 kHz field modulation frequency using a standard rectangular Varian ESR cavity equipped with a Varian nitrogen gas-flow system for temperature control. All ESR spectra were measured at room temperature or at 133 K by using quartz tubes with 3–4 mm inner diameters under vacuum in solvents such as THF, $CHCl_3$, benzene and toluene. The errors for g- and A-parameters of radicals are ± 0.0002 and ± 0.005 G, respectively. The microwave frequency was standardized by comparing with a diphenylpicrylhydrazyl (DPPH) sample of $g = 2.0036$.

Preparation of the Complexes

3,5-di-*tert*-butyl-1,2-benzoquinone, hydroxylamine hydrochloride, PPh_3 and 1,4-bis-(diphenyldiphosphino)butane (dppb), metal acetates and solvents were obtained from Merck and Fluka Chemical Co. Triarylphosphines $P(XC_6H_4)_3$ ($X = m$-Cl, m-CH_3, and p-Et_2N) and $Pd(Acet)_2$ were prepared as described [9a, b]. All other chemicals were reagent grade and used without further purification. The $MQ_2 \cdot 2H_2O$ complexes were prepared by the following methods without isolation of the oxime ligand.

Method A

A slow stream of nitrogen was passed through a stirred solution of hydroxylamine hydrochloride (0.155 g, 2.23 mmole) and pyridine (0.5 mL) heated under reflux in 100 mL isopropanol and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.44 g, 2 mmole) was added as a solid to this solution. The dark-red solution was refluxed by stirring for 40–45 min under a nitrogen atmosphere. A deoxygenated hot methanol solution (10–15 mL) of 1 mmole transition metal(II) acetates was added and the mixture was refluxed under nitrogen for about 1 h. The volume of the resulting mixture was concentrated to ca. 15 mL and the precipitated solid obtained on cooling was collected by filtration, washed with water and a minimal amount of cooled methanol and dried. The compounds were recrystallized from methanol or hexane.

Method B

These complexes were also prepared with a similar procedure as above in air. Hydroxylamine hydrochloride (0.174 g, 2.5 mmole) was dissolved in 100 mL of isopropanol and pyridine (0.5 mL) and refluxed for 5 min, and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.5 g, 2,3 mmole) was added as a solid. The solution was heated by stirring for 40 – 50 min and a 15 mL of methanol solution of metal (II) acetates (1.15 mmole) was added. The resulting solution was refluxed for about 1 h and the volume of mixture reduced by evaporation of solvent to 10 – 15 mL. The precipitated crystals obtained on cooling were filtered, washed with a minimal amount of methanol and crystallized from hot methanol or hexane. By this procedure we also attempted to prepare DTBQ-dioximate complexes using 1 : 2 and 1 : 3 mole ratios of DTBQ and $NH_2OH \cdot HCl$. Reactions of $CuQ_2 \cdot 2H_2O$ and $PdQ_2 \cdot 2H_2O$ with tertiary phosphines and dppb were carried out by mixing their well degassed toluene solutions on a vacuum line; ESR spectra of reaction mixtures were immediately recorded at room temperature. The results of elemental analysis for the complexes prepared under N_2 are summarized in Table I.

Preparation of Oxime Ligand

3,5-di-*tert*-butyl-*o*-benzoquinone-1-monooxime was prepared by adding 0.01 mol of 3,5-di-*tert*-butyl-*o*-benzoquinone to the mixture of hydroxylamine hydrochloride (0.014 mol) and pyridine (4 mL) in isopropanol (100 mL). The mixture was refluxed on a water bath for 2 h. The solution was then concentrated to 1/10th its volume under reduced pressure and cooled to 0°C. The orange oil was separated, washed with water and recrystallized from methanol (yield 65%, elemental analysis showed that the molecular formula is $C_{14}H_{21}NO_2$), m.p. 88°C. IR spectrum in KBr discs,

TABLE I Some physico-chemical and IR spectrum data of DTBQ–Oxime complexes $MQ_2 \cdot 2H_2O$

Compound	Elemental analysis (%)*			IR spectra, cm^{-1}		
MQ_2	C	H	N	$\nu_{C=N}$	$\nu(CO)$	$\nu(H_2O)$
CuQ_2	63.82 (62.74)	7.92(8.21)	5.08(5.23)	1618	1648	3157, 3200
NiQ_2	64.20(63.30)	7.92(8.28)	5.08(5.27)	1620	1642	3420
CoQ_2	63.29(63.52)	8.33(8.28)	5.66(5.27)	1614	1635	3448, 3208, 3157
PdQ_2	59.13 (58.09)	6.97(7.60)	5.19(4.84)	1615	1642	3430, 3248, 3119
MnQ_2	63.34 (63.76)	8.65(8.38)	5.57(5.31)	1604	1635	3397

*Calculated values are given in parentheses.

cm^{-1}: 3240–3250 (OH), 1680 (C=O), 1640 (C=N). ^{1}HNMR, in CDCl$_3$ (δ, ppm): 1.25s (9H), 1.29s (9H); 7.43d (H), 7.83d (H); 11.25s (H). Electronic spectrum, λ_{max} (nm): 207, 240 (sh), 311, 390, 680 (methanol); 324 (ε 8746), 431 (ε 3578), 684 (ε 48) (toluene). The band at 680 nm is assigned to the nitroso tautomer of the oxime ligand [11b]. The electronic spectral data in various polarity solvents indicate that the concentration of the nitroso tautomer in weakly polar solvents is higher than in polar solvents.

RESULTS AND DISCUSSION

Consideration of the elemental analysis, spectral and magnetic moments data of the complexes which were synthesized in air using a 1:2, 1:3 mole ratios of DTBQ and $NH_2OH \cdot HCl$ indicate that our attempts to prepare DTBQ-dioxime complexes were unsuccessful. The analytical data allow us to formulate compounds synthesized with Method A as bis(3,5-di-*tert*-butyl-*o*-benzoquinone-1-monooximato)M(II) dihydrate complexes abbreviated as $MQ_2 \cdot 2H_2O$ (Tab. I).

The UV-visible, IR and ESR spectra of bis(3,5-di-*tert*-butyl-*o*-benzo-quinone-1-monooximato) M(II) compounds synthesized in air were significantly different from those prepared under nitrogen. The main differences these complexes are as follows: (a) in the IR spectra all complexes obtained by Method B have a broad intense band in the 3430–3440 cm^{-1} region which was attributed to ν(OH) stretching frequency for H_2O molecules of crystallization. The positions of these bands remain practically unchanged in the spectra of the complexes, indicating that water molecules are not involved in bonding with metal ions. But the IR spectra of the complexes synthesized by Method A show relatively weak absorption bands in the 3180–3250 cm^{-1} region, which were attributed to stretching vibration, ν(O—H), of coordinated H_2O molecules; (b) the samples of Co(II), Ni(II), VO(II), Pd(II) and Zn(II) compounds synthesized in air except Cu(II) and Mn(II) showed an ESR signal consisting of a superposition of overlapping radical spectra and centered at $g = 2.003–2.005$. In some cases these radical species vary depending on the molar ratio DTBQ and $NH_2OH \cdot HCl$. It is interesting that the radical signals observed for the samples of Co(II), Ni(II) and Pd(II) were essentially identical. At the same time, in case of Method A the radical signal was observed only for Co(II) complex. Finally, all complexes except Cu(II) prepared in air show strong absorption bands($\varepsilon \sim 10^3 – 10^4$ L mol^{-1} cm^{-1}) centered at 280–450 nm and 600–900 nm. In addition, the electronic spectra of these complexes also exhibit

strong solvatochromic effects. These bands and their solvent dependent behavior are characteristic for semiquinonate derivatives of $3d$ metal ions and can be assigned to ligand based $n \rightarrow \pi^*$ or metal-to-ligand charge-transfer ($d \rightarrow \pi^*$) transitions [4, 11 – 15]. Thus, our examination showed that complexation of 3,5-di-*tert*-butyl-*o*-benzoquinone-1-monooxime ligand by the transition metal ions in air along with the formation of bis(oximato) complexes take place by oxidation with atmospheric O_2 which afforded various stable radical species. Note that the observed ESR spectra of radical species mainly consist of superposition at least two signals. Although, the analytical data of complexes obtained in air is agreement with the formulation as $MQ_2 \cdot 2H_2O$ good solubility of the complexes and radicals in polar and nonpolar organic solvents does not allow us to isolate these complexes and radicals in pure form. As a detailed interpretation of the spectra is not possible, we report the complexes synthesized only under N_2 in this paper. The IR data of these complexes are given in Table I.

The similarity of the IR spectra of $MQ_2 \cdot 2H_2O$ in the $700 - 4000 \, cm^{-1}$ region strongly suggests the presence of the same organic ligand in these compounds. The absorption bands in the $1604 - 1620 \, cm^{-1}$ and $1636 - 1648 \, cm^{-1}$ regions assigned to the coordinated $\nu(C=N)$ and $\nu(C=O)$ groups, respectively. The bands observed in the region of 1650 to $1780 \, cm^{-1}$ may be attributed to the deformation vibration of $H \cdots O \cdots H$ hydrogen bonds, $\delta(O \cdots H \cdots O)$, between coordinated H_2O molecule and oxime oxygen in complexes [16].

The electronic spectra of $MQ_2 \cdot 2H_2O$ were recorded in various solvents such as EtOH, $CHCl_3$, dioxane and toluene (Tab. II). As seen in Table II, there are some solvent effects on the spectra of complexes. Similar solvatochromisim is characteristic for semiquinone or catecholato complexes [15, 17, 18]. Note that the 3,5-di-*tert*-butyl-*o*-benzoquinone-1-monooxime (QH) previously has been synthesized and characterized by Ivakhnenko /11b/.

Cu(II) Complexes

The room temperature magnetic moment of $CuQ_2 \cdot 2H_2O$ (1.85 B.M) is typical for mononuclear compounds of Cu(II) with $S = 1/2$ spin state and does not indicate any antiferromagnetic coupling of spins at this temperature.

Electronic Spectra

The electronic spectra of $CuQ_2 \cdot 2H_2O$ were obtained from $10^{-3} - 10^{-4} \, M$ solutions of toluene, chloroform, ethanol and dioxane over the range from

TABLE II Electronic spectrum data for $MQ_2 \cdot 2H_2O$ complexes

Complex	Solvent	Electronic absorption spectra, $\lambda_{max}(\varepsilon \times 10^4 \, L \, mol^{-1} cm^{-1})$, nm
CuQ_2	EtOH	238(2.25), 235(2.34), 263(1.44), 301(1.32), 351(16.8), 429(5.1), 531(6.1)
	Dioxane	238(15.7), 260(11), 308(13.7), 348(10.8), 428(4.8), 528(3.4)
	Toluene	317(1.42), 351(1.44), 441*, 540(5.2)
	Toluene + PPh₃	548, 600(sh), 754, 840(sh)
NiQ_2	EtOH	204(2.84), 237(2.37), 260*, 341(1.59), 497(0.86)
	EtOH + Ph₃	341, 494, 653, 796
	CHCl₃	257(3.15), 270*, 377(3.32), 487(0.76), 612(0.85), 612(0.67), 867*
	CHCl₃ + PPh₃	376, 491, 630, 796
PdQ_2	EtOH	213(4.2), 238(5.8), 258(0.55), 381(0.25), 482(0.2), 560(0.0054), 593(0.08), 650(sh)
	CHCl₃	259(0.81), 312(0.51), 375*, 384(0.52), 420*, 560*, 598(0.082), 682*
	CHCl₃ + PPh₃	315(0.142), 363(1.31), 430*, 560*, 594(0.236), 780
	Toluene	314, 333, 368, 377, 435*, 560*, 590, 620*, 680*, 770*
	Toluene + PPh₃	330*, 356, 540, 640*, 780
CoQ_2	EtOH	205(2.53), 240*, 262(2.34), 364(1.8), 580(0.41)
	CHCl₃	265(2.82), 280*, 368(2.29), 581(0.42)
	Dioxane	250, 261, 364, 430*, 584, 620*
	Toluene	283(2.81), 365(2.72), 420, 520*, 575(0.53), 20, 800**
MnQ_2	EtOH	204(2.84), 236(2.54), 368(1.63), 390(sh), 600(sh), 781(0.3)
	CHCl₃	244(3.77), 320(1.46), 371(4.84), 470*, 620*, 785(0.41)
	Dioxane	246, 320*, 368, 390*, 600*, 781

*Shoulder.
**Very weak and broad shoulder.

200 to 900 nm (Tab. II). Two intense visible bands were observed in the range of $429-440$ ($\varepsilon = 5000-6600 \, \mathrm{L \, mol^{-1} \, cm^{-1}}$) and $528-531$ nm ($\varepsilon = 4000-6000 \, \mathrm{L \, mol^{-1} \, cm^{-1}}$). Owing to the very high molar extinction coefficients of these bands, the observed absorptions cannot be assigned to *d-d* transitions. The intense electronic transition at 530 nm in this complex is assigned to $d \rightarrow \pi^*$ (chelated azomethine-oxime). The band at 440 nm may be due to an intraligand charge transfer electron transition. The absorptions at ca. 300 and 350 nm in polar solvents remain unchanged when the solvent polarity increases in the sequence toluene–dioxane–$CHCl_3$–EtOH. Electronic spectral measurements revealed that solutions of $CuQ_2 \cdot 2H_2O$ did not show any color change in solvents such as benzene, toluene, hexane and $CHCl_3$.

When $CuQ_2 \cdot 2H_2O$ was mixed with an equimolar or excess amount of PPh_3 in toluene or other solvents at room temperature the color changed. Thus when two molar equivalents of PPh_3 were added to one molar equivalent of $CuQ_2 \cdot 2H_2O$ in toluene, benzene, hexane and $CHCl_3$ at 300 K, the brown–violet color of solutions changed to orange. In this case the band at 530 nm disappeared and a new more intense band occurred at 435 nm ($\varepsilon = 10.000 \, \mathrm{L \, mol^{-1} \, cm^{-1}}$ in benzene). In addition, treatment of this complex with a $6-8$ fold excess of PPh_3 the orange solution became approximately colorless after $5-6$ min and the intense band at 435 nm disappeared. In contrast to this, the red color upon addition of $8-10$ fold excess of PPh_3 in THF remains unchanged at least two days in air. In general, the reduction proceeded more readily in nonpolar solvents than in polar solvents.

ESR Spectra

The ESR spectra of $CuQ_2 \cdot 2H_2O$ were recorded in the polycrystalline state as well as in $CHCl_3$ and toluene solutions at 300 and 130 K. The ESR spectrum of the polycrystalline samples of $CuQ_2 \cdot 2H_2O$ shows rhombic symmetry ($g_1 = 2.082$, $g_2 = 2.108$, $g_3 = 2.178$) which indicates the existence of partial mixing of the d_{z^2} orbital into the $d_{x^2-y^2}$ magnetic orbital [19a]. The lack of $\Delta Ms = \pm 2$ forbidden transition (ca. 300 and 130 K) at half-field ($\sim 1600 \, \mathrm{G}$) region indicates the absence of dimer structure in the solid state.

The ESR spectrum of $CuQ_2 \cdot 2H_2O$ in toluene solution at 300 K showed a typical four-line pattern ($g_{iso} = 2.116$, $A_{iso} = 88 \, \mathrm{G}$), due to coupling of the unpaired electron with the nucleus ($I = 3/2$) of copper. Further splitting into four and eight lines of the high field $M_I = 1/2$ and $M_I = 3/2$ components,

respectively, due to the coupling of the unpaired electron to the two nonequivalent ^{14}N ($I = 1$) nuclei ($A^N = 14\,G$) was also observed (Fig. 2a). The frozen solution (130 K) spectrum of the $CuQ_2 \cdot 2H_2O$ ($g_{\Pi} = 2.249$, $g_{\perp} = 2.044$, $A_{\Pi} = 160\,G$, $A_{\perp} = 43\,G$) in toluene exhibits well-resolved superhyperfine structure due to ^{14}N ($A^N = 18\,G$), both on the lowest field component of g_{Π} and in the $g_{\perp}$ regions (Fig. 2b). The trend $g_{\Pi} > g_{\perp} > g_e$ of g-tensors shows that the unpaired electron is in a $d_{x^2 - y^2}$ ground state [19]. The g_{Π}, $g_{\perp}$ and A_{Π} values are close to those reported for a number of distorted-octahedral Cu(II) complexes [19e]. It is interesting that the ESR spectrum of $CuQ_2 \cdot 2H_2O$ shows solvent dependence. The ESR spectrum of the concentrated $CHCl_3$ solution of $CuQ_2 \cdot 2H_2O$ shows an unusual broad signal centered at $g = 2.109$ (Fig. 2c); at the same time, on dilution of this sample with $CHCl_3$ a four-line pattern ($g_{iso} = 2.042$, $A^{Cu}_{iso} = 74\ G$) without ^{14}N-shfs spectrum is observed (Fig. 2d).

By mixing a molar equivalent or excess of PPh_3 with $CuQ_2 \cdot 2H_2O$ in toluene the four-line ESR spectrum of Cu(II) disappeared immediately and a new complex multiplet pattern centered at $g = 2.004$ was observed (Fig. 3a). The central part of the spectrum recorded immediately after reduction, consists of a doublet (1.75 G) of quartets (peak-to-peak separation of 0.625 G) and triplet (1.75 G) of relatively resolved multiplets. Each triplet has small but observable shifts (0.18 G) attributed to the protons of the *tert*-butyl groups. The coupling constants associated with these triplets were attributed to one nitrogen ($I = 1$) and nine protons of the *tert*-butyl group. This spectrum is similar to that of previously reported aminosemiquinonetype radicals [20]. Attempts to resolve the external doublet spacing of 1.25 G and singlet using a small modulation amplitude, a small gain and scan time didn't improve the resolution of this signal. It should be noted that after 30–40 min the resolution of the spectrum degrades and the observed spectrum is very similar to those obtained for the $Cu(Q)_2 - P(PhX)_3$ systems (Fig. 3b). It is interesting that the ESR spectra of $CuQ_2 \cdot 2H_2O - P(XC_6H_4)_3$ ($X = m$-Cl, m-CH_3, p-Et_2N—) and $CuQ_2 \cdot 2H_2O - dppb$ systems recorded in a toluene/$CHCl_3$ mixture and at room temperature are essentially similar to those for the $CuQ_2 \cdot 2H_2O - PPh_3$ system, but some central multiplets were incompletely resolved. These spectra can be compared to a theoretical spectrum of singly oxidized [(6′-oxo-3′,5′-di-tert-butylcyclohexa-2′,4′-dien-1-ylideneamino)-4,6-di-tert-butyl-o-benzosemiquinone] [11] which would have 29 lines if the unpaired electron interacted with one nitrogen and two sets of two equivalent hydrogens. All ESR spectra of $CuQ_2 \cdot 2H_2O -$ triphenylphohisphine systems (Figs. 3 and 4) mainly have 29 resolved lines, several of which show additional unresolved
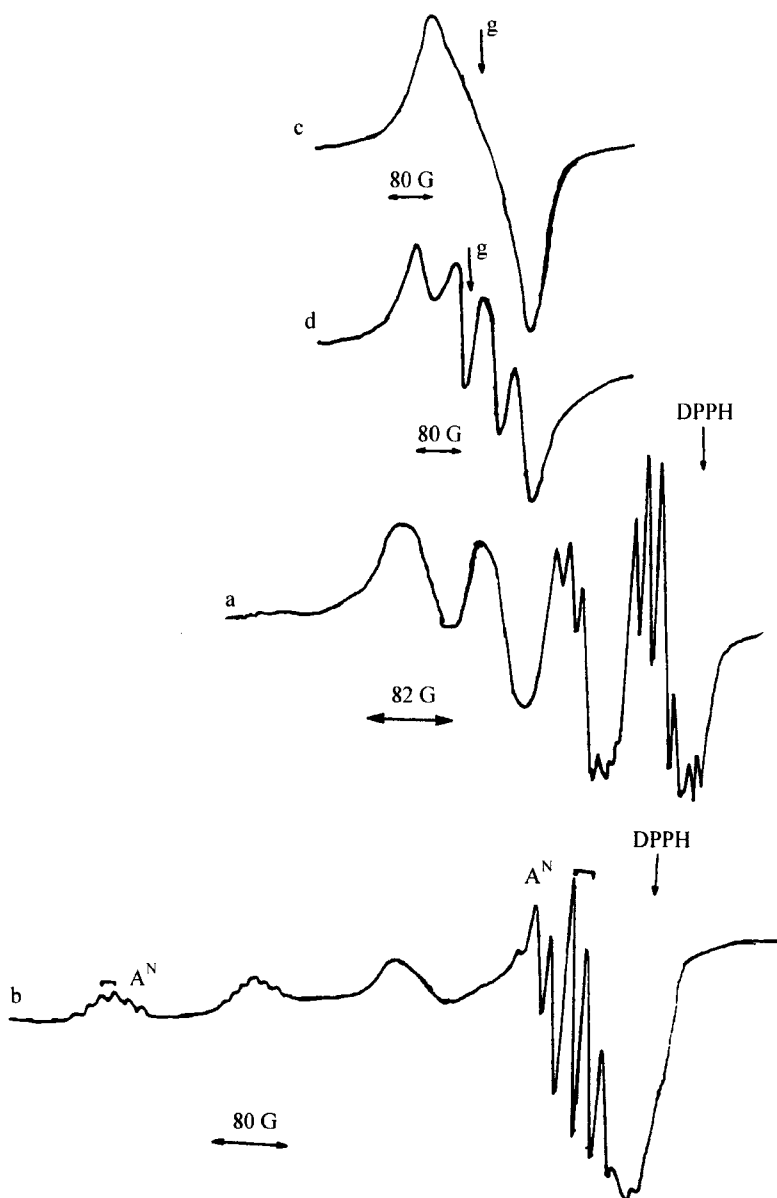
FIGURE 2 The ESR spectra of $CuQ_2 \cdot 2H_2O$ at 300 K (a) and 130 K (b) in toluene; in concentrated (c) and diluted (d) $CHCl_3$ solution at 300 K.

splittings attributed to the protons of the *tert*-butyl groups. These spectra were analyzed in terms of an interaction of the unpaired electron with one nitrogen ($A^N = 7.4$ G) and two sets of two hydrogens [$A^H = 3.5$ G (2H)

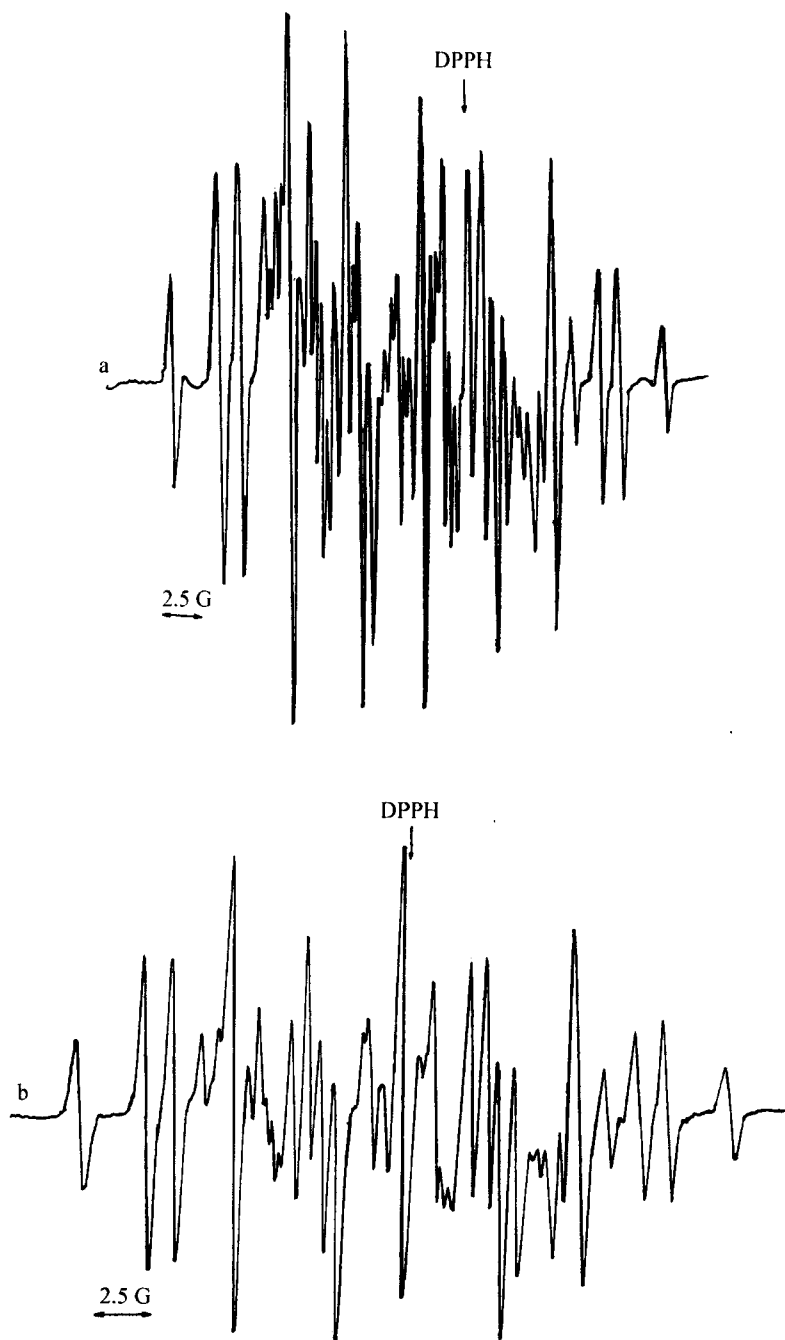FIGURE 3   ESR spectra of reaction mixture of $CuQ_2 \cdot 2H_2O$ with PPh_3 in toluene at 300 K in the initial stage (a) and after 40 min (b).

DPPH
↓

a

3.85 G

DPPH
↓

b

3.85 G

DPPH
↓

c

7.4 G
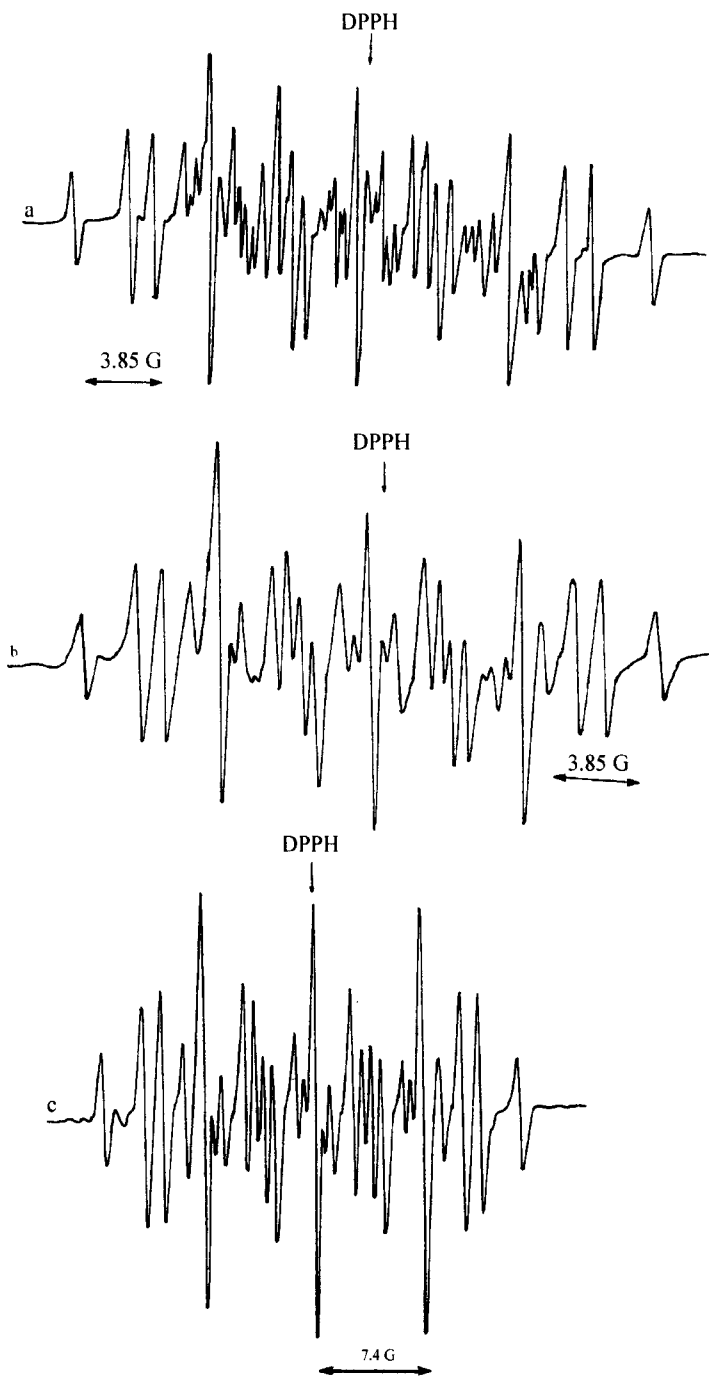
FIGURE 4   ESR spectra of the $CuQ_2 \cdot 2H_2O$ + triarylphosphine systems at 300 K in toluene: $CuQ_2 \cdot 2H_2O$ + dppb (a); $CuQ_2 \cdot 2H_2O$ + $(m\text{-}CH_3C_6H_4)_3P$ (b); $CuQ_2 \cdot 2H_2O$ + $(m\text{-}ClC_6H_4)_3P$.

and 1.75 G (2H)]. Unfortunately, our attempts to separate these radical mixtures by chromatography were unsuccessful because of their unstability under air.

The reactions studied can be accounted as indicated in Scheme 1. In the initial stage the reduction of the complex gives the quinone oximato bis(triarylphosphine)copper(I) complexes (1) and the ligand radical (2) which affords the nitrene species (3) and (4) *via* deoxygenation and hydrogen abstraction reactions, respectively.

Previously Charalambous and co-workers [21] proposed that reduction of bis(1,2-benzoquinone-monooximato)Cu(II) complexes with PPh$_3$ proceeds *via* a radical intermediate, but they didn't have any ESR evidence confirming the presence of radical species in these reaction mixtures.

Complexes of Mn(II)

Complexes MnQ$_2 \cdot$ 2H$_2$O synthesized under air and N$_2$ have identical elemental analyses, IR, electronic spectral, ESR and magnetic moment data, and their ESR spectra didn't show radical signal. Here we described the complex obtained under N$_2$. The magnetic moment of MnQ$_2 \cdot$ 2H$_2$O in the solid state was found to be 4.49 B. M. at room temperature. This value is below the spin only value for high-spin ($S = 5/2$, $\mu_{eff} = 5.92$ B. M.) Mn(II) and well above that for low-spin ($S = 1/2$, $\mu_{eff} = 1.73$ B. M.) octahedral complexes. While the observed magnetic moment is typical of a magnetically dilute high spin d^4 manganese(III), the formation of a Mn(III) complex is ruled out according to its elemental analysis, IR and ESR spectra (ESR spectra of d^4 ions exhibit an axial signal with $g_{\Pi} = 2$ and $g_{\perp} \approx 4$ [24c]). However, the observed subnormal magnetic moment of this complex may be interpreted in terms of a spin-equilibrium between the high-spin ($S = 5/2$)

SCHEME 1

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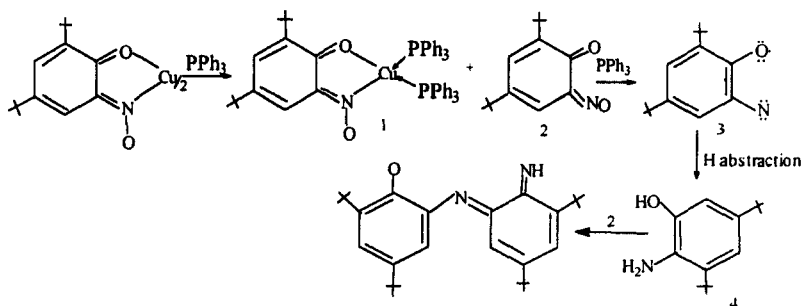
and low-spin $(S = 1/2)$ states, in which both spin doublet and spin sextet states are occupied at room temperature [24a]. The isotropic ESR spectra of this complex in toluene and THF solutions recorded at 300 K exhibit the typical ^{55}Mn $(I = 5/2)$ d^5 six-line signal spacing of 92.5 and centered at $g = 2.072$ (Fig. 5a). No significant changes were observed in either the g_o or A_o isotropic values in various solvents. At the same time, the compound $MnQ_2 \cdot 2H_2O$ exhibits essentially identical ESR spectrum in the solid state at room temperature and frozen solution in THF at 130 K (Fig. 5b). This fact implies that complex possesses identical environment around Mn(II) in the frozen solution and solid states. As seen from Figure 5b solid state and frozen-solution $(g = 2.046$ and $A^{Mn} = 120 \text{ G})$ spectra of $MnQ_2 \cdot 2H_2O$ consist of two superimposed slightly shifted six-line patterns. These spectra are very similar to that of hexacoordinated Mn(II) complexes with a N_4O_2
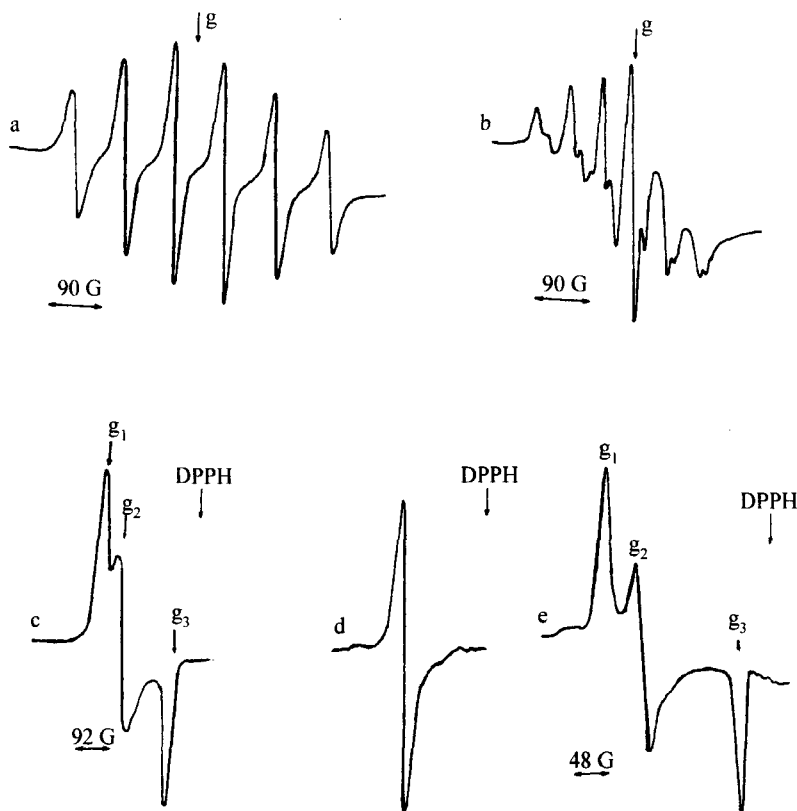

FIGURE 5   ESR spectra of $MnQ_2 \cdot 2H_2O$ in THF at 300 K (a) and 130 K (b); (c) solid state (300 K), in THF at 300 K(d) and 130 K (e) of $NiQ_2 \cdot 2H_2O$.

donor set [24b]. The observed splitting of the manganese hyperfine structure in the solid state and in the frozen THF glassy ESR spectra may be associated with two different isomers of this complex both in the solid state and in the frozen solution states. It is necessary to note that a similar ESR spectral feature has been obtained from a binuclear mixed-valence $Mn_2^{II,III}$ complex comprised of essentially uncoupled manganese-(II) and -(III) ions [24d].

Ni(II) Complexes

An ESR spectrum of $NiQ_2 \cdot 2H_2O$ obtained under air exhibits a low intensity radical multiplet pattern having identical magnetic-resonance parameters found for $Co(Q_x)_2$ (Fig. 6a). A sample of $NiQ_2 \cdot 2H_2O$ synthesized under N_2 did not show radical signal. The magnetic moment (3.29 B. M.) of this complex corresponds to the values typical for Ni(II) in a high-spin octahedral environment [23a]. The magnetic moment value is
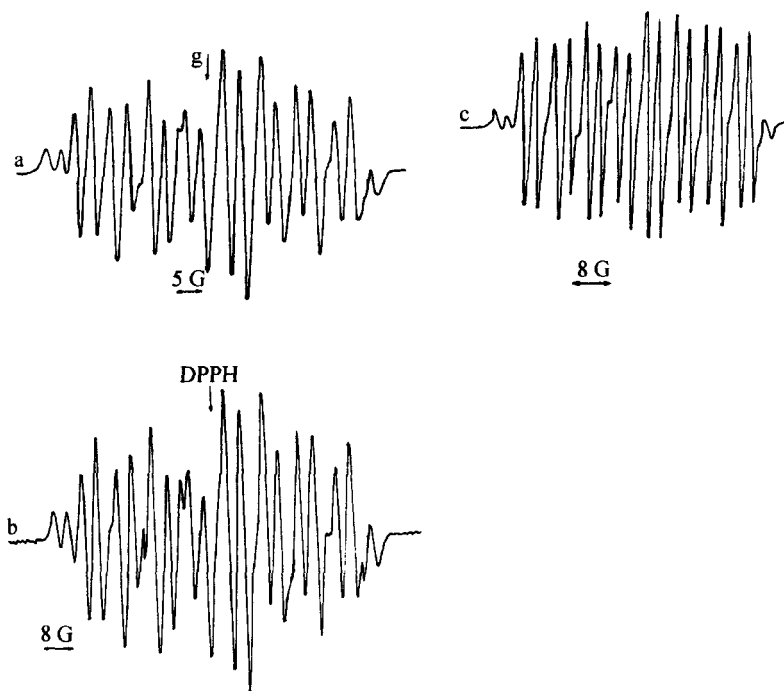

FIGURE 6 ESR spectra of $CoQ_2 \cdot 2H_2O$ prepared in air at 300 K in toluene (a), of $CoQ_2 \cdot 2H_2O$ prepared under N_2 (b), after performing a high-temperature study on a sample of $CoQ_2 \cdot 2H_2O$ synthesized in air (c).

higher than the spin-only value of 2.83 B. M. for two unpaired electrons, which is typical for d^8 due to spin-orbit coupling [23]. It is interesting that, unexpectedly, the solid state sample of this complex at room temperature exhibits an ESR spectrum corresponding to a rhombic pattern without additional ^{14}N-splitting (Fig. 5c), which differs from the ESR signal of Ni(III) [23b] and radical species. The observation of an ESR signal of Ni(II) complexes at room temperature is rare; similar behavior has previously been observed for some octahedral Ni(II) complexes [23c, d]. The principal g-values of the powder sample at room temperature are as follows: $g_1 = 2.187$, $g_2 = 2.144$, $g_3 = 2.052$. At the same time, the isotropic spectrum in toluene or $CHCl_3$ solutions at 300 K shows a symmetric singlet centered at $g = 2.134$ which is equal to the average $\langle g \rangle$ of three principal g_1, g_2, and g_3 values $[\langle g \rangle = 1/3(g_1 + g_2 + g_3)]$ (Fig. 5d). Additional superhyperfine splitting assignable to the equatorial nitrogens was not observed. The frozen-glass ESR spectrum (Fig. 5e) recorded in $CHCl_3$ or toluene at 113 K also shows a rhombic pattern of principal g-values ($g_1 = 2.194$, $g_2 = 2.157$, $g_3 = 2.037$) which slightly differ from those for the powder sample. It is known that in an octahedral field, the ground state of Ni(II) is $^3A_{2g}$ and the spin-orbit coupling does not split into the $m_s = 0$ and $m_s = \pm 1$ level and thus an ESR spectrum is not observed if it is not done at lower temperature. But in rare instances, for distorted octahedral Ni^{+2} centers having a moderate amount of zero-field splitting, it is possible to observe the ESR spectrum at room temperature. Thus the detected spectrum is one of the rare cases where the orthorhombic ESR spectrum is observed at room temperature. Another interesting feature of $NiQ_2 \cdot 2H_2O$ was observed when its $CHCl_3$ solution was treated with PPh_3. By mixing $CHCl_3$ and toluene solutions of $NiQ_2 \cdot 2H_2O$ with PPh_3 the color changed from reddish (λ_{max} at 257, 270, 377, 487, 612, 857 nm) to brown−green with maxima at 341, 495, 630, 790 nm. The ESR examination of this reaction mixture at room temperature shows that the symmetric singlet at 2.134 disappears and a new low intensity radical singlet centered at $g = 2.0025$ appears which is also stable in air. The degassed sample of this mixture shows a less resolved 18-lined multiplet with hfsc of ca. 0.75 G.

Co(III) Complexes

Magnetic moments of the cobalt complexes prepared by both Methods A and B were subnormal low (~ 1.2 B. M.) which indicates, formation of Co(III) compounds. Unfortunately, our attempts to isolate a pure sample of these products have been unsuccessful because of their solubility. It is
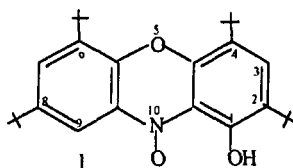
SCHEME 2

interesting that the samples of Co(III), Ni(II) and Pd(II) which were synthesized in air, unlike Cu(II) and Mn(II) show quite similar room-temperature isotropic ESR spectra centered at $g = 2.0034$ and consist of 19 hyperfine lines (Fig. 6a). The central region of this spectrum consists of well-resolved almost equal intensity octet (8.2 G) of doublets (3.4 G), and on each side of the octet pattern there are low intensity doublet lines. Some lines of the spectrum show additional poorly resolved hyperfine structure, most probably arising from protons of *tert*-butyl groups. The unique property of this radical species is its unreactivity towards air oxygen. Surprisingly, in contrast to Ni(II) and Pd(II) ions, the sample of Co(II) synthesized under N_2, also exhibits an ESR signal centered at $g = 2.0025$ (Fig. 6b) which is very similar to that of complex Co(III) obtained in the air. In the central part of this spectrum is clearly seen the octet (8.1 G) of equally spacing doublets (3.4 G). The generation of radical species for Co(II) compound prepared in the absence of O_2, undoubtedly, indicates that the complexation of oxime ligand by Co(II) is accompanied by a one-electron transfer from Co(II) to oxime. The observation of quite similar spectra for various metal-containing systems indicates that the generated radical species are not involved in bonding with metal ions. Note that the observed ESR signals remains unchanged over the period of four years in the solid state and more than 3−4 months in solution. Unfortunately, it is too diffcult to give the exact interpretation for the observed spectral patterns because of the complexity of the spectrum. But, on the basis of stability, the observed spectral pattern may be attributed to 1-hydroxy-2,4,6,8-tetra-*tert*-butyl-phenoxazine-10-oxyl radical (*I*). In this case, the experimental spectrum could be analyzed by assuming that the unpaired electron interacts with one nitrogen ($A^N = 24$ G) and two sets of four hydrogens [$A^H = 8.2$ G (3 H) and 3.4 G (1 H)].

The observed spectral features in Co(II)−QH system are quite different from those of aminosemiquinone [20], phenoxazine [22a, 25], benzosemiquinone iminate [11], semiquinones [2, 4, 15, 26] and aminophenoxyl [22a, c] type radicals.

The spectra of radicals obtained in air was also studied over a wide range of temperatures. The spectrum of this sample was recorded in 10°
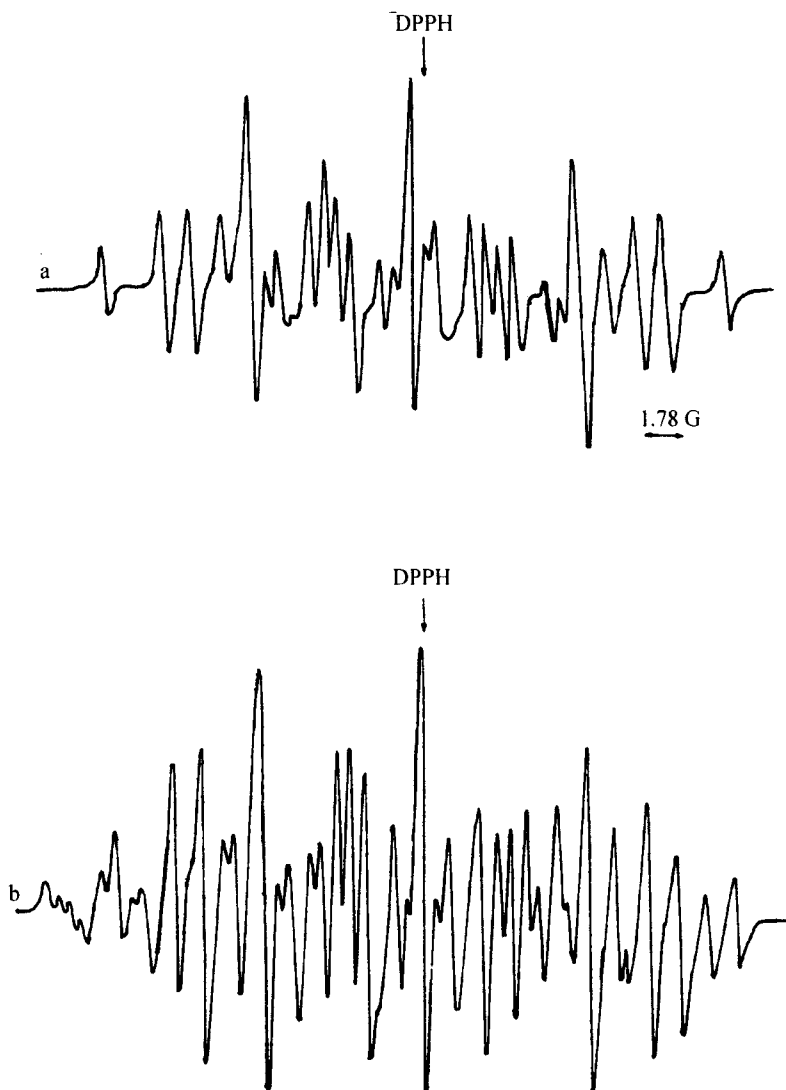
FIGURE 7   ESR spectra of reaction mixture of $PdQ_2 + PPh_3$ in toluene at 300 K (a) and oxidizing sample of PdQ_2 in toluene at 300 K (b).

increments from 20 to $+100°C$ (in toluene). No changes in the isotropic coupling constants of the radical were observed over these temperatures. On keeping this sample at 100°C for 40 min and after cooling the solution to 20°C, dissociation of the radical did not occur. Figure 6c shows the isotropic room-temperature spectrum of this radical obtained after performing a

high-temperature study on a sample of Co(III) synthesized in air. This spectral pattern is invariant with changes in complex concentration over the range of 10^{-4}–10^{-3} mol L^{-1} as well as with changes in modulation amplitude from 0.05 to 2 G.

Finally, note that CoQ_2 was purified by silica gel column chromatography with a solvent system of hexane–chloroform and no change in electronic and ESR spectra of this sample were observed.

Complexes of Pd(II)

The ^{1}H NMR spectrum of PdQ_2 in $CDCl_3$ shows two intense sharp peaks at 1.27 and 1.44 ppm as well as equal intensity low-field resonances at 6.96 and 7.51 ppm. These higher field and lower field doublets integrate 9:1 with respect to each other. Integration values obtained from the NMR spectrum indicate that the upfield and downfield doublet resonances can be assigned to the *tert*-butyl groups and benzene ring protons, correspondingly.

When toluene solutions of $PdQ_2 \cdot 2H_2O$ and PPh_3 are mixed at room-temperature the green color with λ_{max} at 333, 368, 377, 594 ($\varepsilon =$ 2360 L mol^{-1} cm^{-1}) and slight shoulders at ~440, 560, 625, 680, 770 nm turn into dark violet with maxima at 314, 357, 505, 774 nm with shoulders at ~570, 620 nm. These data show that on reduction along with disappearance of some shoulders, the broad asymmetric maximum at 594 nm shifted to 540 nm and new maxima appeard at 357, 505 and 774 nm. The ESR spectrum recorded immediately after mixing toluene solutions of $PdQ_2 \cdot 2H_2O$ and PPh_3 at 300 K shows a complex multiplet pattern centered at $g = 2.0046$ (Fig. 7a). This spectrum consists of nine sets of doublets with spacing of 1.25 G and an unresolved singlet at both ends. The spectrum exhibits a central, complicated, poorly resolved set of five multiples with spacing of 2.25 G. Each line of the doublet and triplet is further split into four lines (0.5625 G) with relative intensity ratios of 1:1:1:1 and incompletely resolved five lines (0.5625G), respectively. The observed ESR spectrum involved a less resolved complex splitting pattern and exact interpretation would be very difficult. Surprisingly this spectrum is identical with the spectra of $CuQ_2 \cdot 2H_2O$-phosphine systems and they undoubtedly arise from the same radical species. No additional splittings were observed on the central multiplet, even at modulation amplitudes as low as 0.1 G. This radical appeared to be stable at room temperature and under vacuum three days as shown by ESR. Note that in the process of the reduction of $PdQ_2 \cdot 2H_2O$ no precipitation of metallic Pd^0 was observed.

$PdQ_2 \cdot 2H_2O$ is sensitive to air. After recrystallization of $PdQ_2 \cdot 2H_2O$ from hexane under air, its ESR spectrum at room temperature in toluene shows a complex multiplet signal centered at $g = 2.004$ (Fig. 7b) and has twenty-nine resolved lines, several of which show additional unresolved splittings. This spectrum reflects superposition of two signals and differs from the spectrum of the reduced $PdQ_2 \cdot 2H_2O$ samples. Treatment of this sample with PPh_3 under vacuum has an observed ESR spectrum which is essentially identical with those in Figure 4. Note that our attempts to separate radical mixtures by column chromatography for the Pd—PPh_3 system were unsuccessful because of their instability.

Thus the fact that reduction of Cu(II) and Pd(II) complexes with various tertiary phosphines gave practically the same spectral pattern, indicates that the formed radical species didn't contain any phosphine molecules and metal ions. On the other hand, the observation of the transformation of the initial spectrum of the $CuQ_2 \cdot 2H_2 O$—PPh_3 system and the spectrum of the oxidized $PdQ_2 \cdot 2H_2O$ sample in the presence of PPh_3 to the ESR signal which is common for $CuQ_2 \cdot 2H_2O$—$P(XC_6 H_4)_3$ systems can be taken as an evidence that these spectra are due to secondary radical species. Note that the observed spectral patterns are different from the spectra of phenoxazine [22], amino-semiquinone [20] and amino phenoxy [22] type radicals, but they are very similar to the spectra of N-(2'-hydroxy-3,5-di-tertbutylphenyl)-4',6'-di-tertbutyl-*o*-benzosemiquinone iminate [11]. The observed radical species in the complexation of oxime ligand by Co(II) ions under N_2 and in air, according to their high stability are assigned to a phenazinyl type anion radical.

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