Oxidative Addition of Quinones to Planar Cobalt(II) Dithiolato, Dithioacetylacetonato and Schiff-base Complexes

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Abstract

The reactivity of *ortho*- and *para*-quinones with various four-coordinated planar Co(II) complexes was investigated. The *o*-quinones add oxidatively, producing Co(III) complexes containing chelated *o*-semiquinone radical-anions. No coordination of the fifth ligand in the axial position is involved in these reactions. The reaction between *o*-quinones and Co(II) dithiolates represents the first known example of oxidative addition to Co(II) dithiolato complexes. All observed oxidative additions are reversible; the position of the equilibrium depends strongly on the nature of the equatorial ligand. The extent of radical adduct formation decreases in the order: dithioacetylacetonate > Schiff bases > dithiolates. When redox potentials of the reacting species are changed in a way that makes simple electron transfer between Co(II) complexes and quinones thermodynamically possible, the reduction of quinones to free semiquinone radical-anions becomes competitive with the oxidative addition. In the case of *p*-quinones, only electron transfer is observed if the thermodynamic conditions are met. The structural factors determining quinone reactivity are briefly discussed.

Introduction

Recently, the reactivity of *ortho* and *para* quinones with various structural types of transition metal complexes has been studied in this laboratory [1–9] aiming at the elucidation of the influence of the structure of metal complexes on their redox reactivity. Quinones were chosen as substrates due to their oxidizing as well as coordinating properties, the latter being much more pronounced in their one-electron reduced forms, *i.e.*, in semiquinone radical-anions. Importantly, quinones are able to oxidize transition metal complexes by both electron transfer [1, 2, 10] and oxidative addition [3–10]

mechanisms depending on the properties of particular metal complex.

The one-electron oxidative additions of quinones may also be easily employed to trap various unstable species, e.g., photochemical intermediates. Metal-centered photogenerated radicals like $Mn(CO)_5\cdot$, $CpTiCl_2\cdot$ or strong Lewis acid $Cr(CO)_5$ have been trapped in this way by quinones [2, 7–9]. Obviously, detailed mechanistic studies of these reactions together with a full understanding of relevant structure-reactivity relationships can yield valuable information on the structure and chemical properties of various unstable metal complexes which may be generated photochemically or electrochemically and trapped by quinones either concomitantly or subsequently to their generation. Moreover, the one-electron oxidative additions of quinones produce semiquinone radical complexes with interesting structural, magnetochemical, spectral and chemical properties [3, 4, 11, 12].

Complexes of Co(II) are well known to add oxidatively various substrates, such as O_2, RNO_2, RX or halogens, producing corresponding Co(III) species. We have already studied in detail the oxidative addition of quinones to the square-pyramidal $Co(CN)_5^{3-}$ complex in aprotic media [3, 4]. Both *ortho*- and *para*-quinone isomers have been found to react with $Co(CN)_5^{3-}$ by an identical mechanism. They add oxidatively to the Co(II) central metal atom by only one oxygen donor atom producing Co(III) semiquinone complexes. In the case of *o*-quinones, the oxidative addition step is followed by slow intramolecular substitution of one CN^- ligand by the uncoordinated semiquinone oxygen atom closing the [Co(III)(*o*-semiquinone)] chelate ring. An analogous mechanism operates in the case of the reactions between *o*-quinones and the photogenerated $Mn(CO)_5\cdot$ radical, which is isostructural and isoelectronic with $Co(CN)_5^{3-}$ [2, 13]. The oxidative additions of quinones to d^7-metal centered radicals may be rationalized by the orbital matching scheme [3–5] based on the assumption of parallel orientation of the basal plane of the square-pyramidal

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complex and of the quinone molecular plane. The singly occupied d_{z^2} metal orbital interacts with π^* LUMO of the quinone via its oxygen $2p_z$-component. This interaction is responsible for Co–O σ-bond formation as well as for concerted electron transfer.

Reactions between some Co(II) Schiff-base complexes and quinones have already been observed [14–18] and employed for the synthesis and characterization of the resulting Co(III)–*o*-semi-quinone radical complexes. Although the synthetic reactions described in the literature are usually carried out in THF, the reaction apparently takes place even in noncoordinating hydrocarbon solvents [17, 18].

These planar Co(II) complexes possess the d_{yz}^1 ground-state configuration, the d_{z^2}-orbital being doubly occupied and low-lying [19]. The afore-mentioned orbital matching scheme derived for $Co(CN)_5^{3-}$ is obviously not applicable to planar Co(II) complexes for symmetry reasons. Moreover, certain types of these complexes may also be simply oxidized by electron transfer [20, 26].

These considerations show that the mechanistic study of reactions between quinones and various types of planar Co(II) complexes in noncoordinating solvents as well as in the presence of potential ligands may reveal more information on the detailed mech-anism of the oxidative additions of d^7-complexes as well as on the factors determining the electron trans-fer *vs.* oxidative addition reactivity. We have thus undertaken a systematic investigation of the reac-tions of quinones with various square-planar Co(II) complexes possessing different electron structures, oxidation potentials and abilities to add fifth axial ligands, *i.e.*, with Co(sacsac)$_2$, three different Co-(dithiolato)$_2^{2-}$ complexes and two common Co-(Schiff-base) complexes, namely Co(acacen) and Co(salen), in toluene and in coordinating solvents.

R = CN, mnt^{2-}
R = CF$_3$, pfmdt^{2-}

tdt^{2-}

sacsac$^-$

p - DBQ

o - DBQ
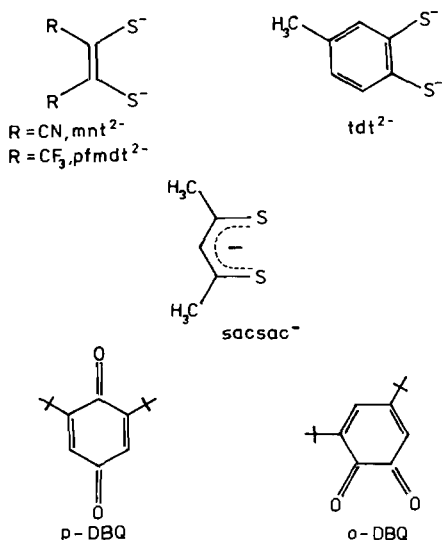
The well-coordinating di-tert-butyl derivatives of *ortho*- and *para*-benzoquinones (*o*-, *p*-DBQ) as well as their strongly oxidizing tetra-chloro analogues have been used in this study*.

Experimental

The Schiff-base complexes N,N'-ethylene-bis-(acetylacetoniminato)cobalt(II), Co(acacen); N,N'-ethylene-bis(salicylideneiminato)cobalt(II), Co(salen); as well as dithiolato complexes bis-maleonitrile-dithiolato cobalt(II), $[Bu_4N]_2[Co(mnt)_2]$; bis-maleonitriledithiolato cobalt(III) dimer, $[Bu_4N]_2$-$[Co(mnt)_2]_2$, bis-(toluene-1,2-dithiolato)cobalt(III), $[Bu_4N][Co(tdt)_2]$, were synthesized by standard procedures [21–25]. The cobalt complex bis-(1,1,1,4,4,4-hexafluoro-2,3-dithiolato-2-butene) co-balt(III) dimer, $[Et_4N]_2[Copfmdt_2]_2$, (or simply bis-(perfluoromethyldithiolato)cobalt(III) dimer) was obtained from Prof. J. A. McCleverty, University of Birmingham. Bis-(dithioacetylacetone)cobalt(II), Co(sacsac)$_2$, was received from Prof G. A Heath, University of Edinburgh.

Strongly air-sensitive solutions of dianionic Co(II) dithiolates Co(tdt)$_2^{2-}$ (brown–green) and Co-(pfmdt)$_2^{2-}$ (red) were prepared by electrochemical reduction of DMF solutions of $[Bu_4N][Co(tdt)_2]$ and $[Et_4N]_2[Co(pfmdt)_2]_2$, respectively.

The *para*-quinones 2,6-di-tert-butyl-1,4-benzoqui-none (*p*-DBQ, Aldrich), 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-CQ, Fluka) and 1,4-benzoquinone (*p*-BQ, Fluka), were purified by vacuum sublimation.

The *ortho*-quinones 3,5-di-tert-butyl-1,2-benzo-quinone (*o*-DBQ, EGA-Chemie) and 3,4,5,6-tetra-chloro-1,2-benzoquinone (*o*-CQ, Fluka) were re-crystallized from heptane or used as received, re-spectively.

The toluene (Lachema) was repeatedly stirred vigorously with H_2SO_4 then with H_2O and $CaCl_2$, and then distilled from P_2O_5 and finally from LiAl-H_4. N,N'-dimethylformamide, DMF (Merck), was refluxed with benzene and water and finally distilled under reduced pressure of nitrogen. The oxygen and moisture-free tetrahydrofuran, THF, was distilled from the sodium metal–benzophenone mixture under argon atmosphere directly to a closed burette, which was then used to transfer pure solvent to a Schlenk-type apparatus. Pyridine (Merck) was dis-tilled from KOH.

All reactions were carried out under argon at-mosphere using Schlenk-technique. The ESR or spectral cells were filled under argon by use of syringes. All experiments were performed at labora-tory temperature.

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*Reduced forms of quinones, *i e.*, the semiquinone radical-anions Q$^-$, are denoted SQ, e g., DBSQ, CSQ

ESR spectra were measured on a Varian E-4 X-band instrument. The 2,2'-di-phenyl-1-picryl-hydrazyl, DPPH, was used for the measurement of g-values (g = 2.0037). A Carl Zeiss Jena M-40 spectrophotometer was employed to measure UV-Vis absorption spectra. Polarographic measurements were performed using LP-7e polarograph with potentiostat modified according to an LP-9 instrument. All electrode potentials are referred to an Ag/AgCl electrode whose potential was determined as +40 mV vs SCE. Preparative electrolyses were carried out on a stirred mercury-pool-electrode at controlled potentials which were set to values corresponding to the limiting currents of the first polarographic reduction waves. 10^{-1} M Bu_4NPF_6 ground electrolyte was used in all electrochemical experiments.

Results

The reactions of Co(sacsac)$_2$ and Schiff-base Co(II) complexes, which are able to add fifth axial ligands, were carried out in carefully purified toluene. The ionic dithiolene complexes are insoluble in toluene. Hence, their reactions were studied in DMF or THF. However, these complexes do not coordinate the solvent molecule [25, 26] so that the axial coordination presents no problem.

The ESR spectra of the 10^{-3} M solutions of Co-(acacen), Co(salen) and Co(sacsac)$_2$ in toluene containing $1-2 \times 10^{-3}$ M o-DBQ exhibit characteristic signals (see Fig. 1) split to eight doublets due to one ^{59}Co ($I = 7/2$) and one ^{1}H nuclei, respectively. The g-values are somewhat lower than those of the free o-DBSQ radical-anion. The ESR parameters
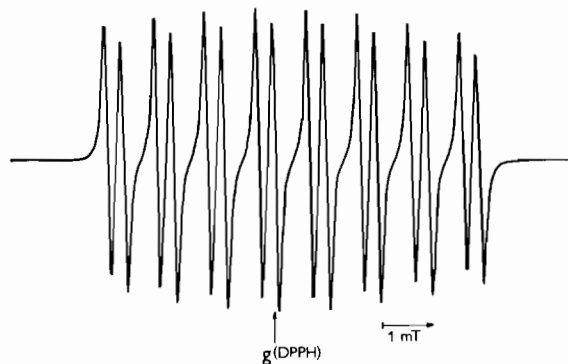

Fig 1 ESR spectrum of [Co(sacsac)$_2$(o-DBSQ)] produced by reaction of 10^{-3} M Co(sacsac)$_2$ with 1.5×10^{-3} M o-DBQ in toluene.

are summarized in Table I. These ESR signals possess all features characteristic for Co(III) complexes containing chelated o-DBSQ radical anionic ligand [3, 4, 15−18, 27] and may be directly attributed to the [Co(acacen)(o-DBSQ)], [Co(salen)(o-DBSQ)] and [Co(sacsac)$_2$(o-DBSQ)] species. The o-DBSQ adducts of the Schiff-base Co(II) complexes are completely stable, whereas the [Co(sacsac)$_2$(o-DBSQ)] undergoes slow decomposition.

Analogous stable Co(III) complexes containing chelated o-DBSQ radical-anionic ligand were found to be formed by the reaction of Co(mnt)$_2^{2-}$ and Co(pfmdt)$_2^{2-}$ with o-DBQ in DMF or THF§ producing [Co(mnt)$_2$(o-DBSQ)]$^{2-}$ and [Co(pfmdt)$_2$(o-

§4 × 10^{-3} M solutions of Co(II)dithiolates with quinone in 5−10 fold molar excess were usually used. The radical complexes are formed in THF in much lower concentration than in DMF

TABLE I ESR Parameters of the Semiquinone Radical-anions and of their Complexes with Co(III)^a

Compound	Toluene			DMF		
	g	a_{Co}	a_H	g	a_{Co}	a_H
o-DBSQ	2.0046^b		0 27^b	2.0047^c		0.315^c
p-DBSQ				2 0052^c		0.214^c
o-CSQ	2.0063^b			2.0062$^{c, e}$		
[Co(sacsac)$_2$(o-DBSQ)]	2.0013	0.99	0.325	2.0016	0.99	0 320
[Co(mnt)$_2$(o-DBSQ)]$^{2-}$				2.0035	1.15	0.30
[Co(pfmdt)$_2$(o-DBSQ)]$^{2-}$				2.0055^d	1.19^d	0 29^d
[Co(acacen)(o-DBSQ)]	2.0017	1.10	0.32	2.0019^e	1.11^e	0.32^e
[Co(acacen)(o-CSQ)]	2.0053	1.18			1.27	
[Co(salen)(o-DBSQ)]	2.0010	1.05	0.33	2.0013^e	1 06^e	0.33^e
[Co(acac)$_2$(o-DBSQ)]		1.10^f	0.345^f		1.10$^{e, f}$	0.345$^{e, f}$
[Co(CN)$_5$(o-DBSQ)]$^{3-}$ ^{g}				2.0044	0.257	0 228
[Co(CN)$_4$(o-DBSQ)]$^{2-}$ ^{h}				2 0026	0.89	0 31
[Co(CN)$_5$(p-DBSQ)]$^{3-}$				2.0050	0.244	0.14

^{a}a Values in mT. estimated accuracy ± 0.005 mT (for complexes); g values determined with accuracy ± 0 0001 ^{b}Na$^+$·SQ ion-pairs prepared by the reduction of Q with sodium amalgam. ^{c}Electrochemically generated in the presence of 10^{-1} M Bu$_4$NPF$_6$. ^{d}10^{-1} M Bu$_4$NPF$_6$ present ^{e}In THF solution. ^{f}Ref 31. ^{g}Monodentate o-DBSQ ligand, ref 4 ^{h}Bidentate o-DBSQ ligand (as in all other complexes referred to in this paper); see ref. 4.
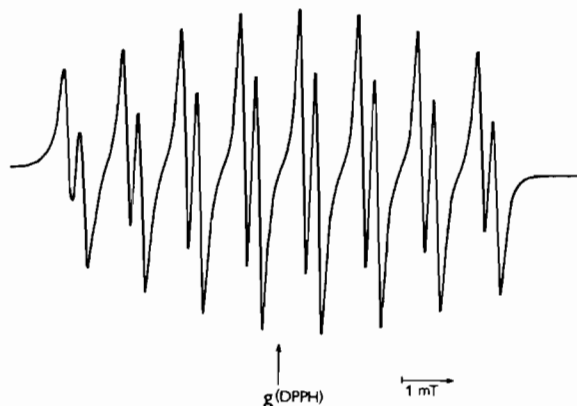
Fig. 2. ESR spectrum of $[Co(mnt)_2(o\text{-}DBSQ)]^{2-}$ produced by reaction of 4×10^{-3} M $[Bu_4N]_2[Co(mnt)_2]$ with 2×10^{-2} M o-DBQ in THF

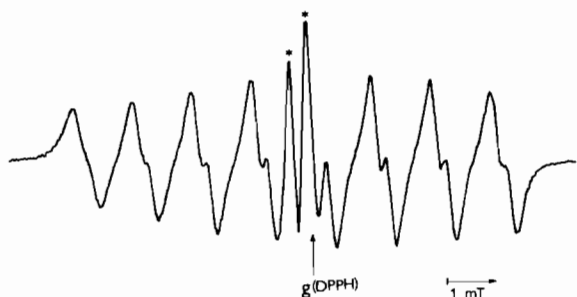Fig 3. ESR spectrum of $[Co(pfmdt)_2(o\text{-}DBSQ)]^{2-}$ and free o-DBSQ. both species produced simultaneously by the reaction of 4.3×10^{-3} M $Co(pfmdt)_2^{2-}$ with 6×10^{-2} M o-DBQ in 10^{-1} M Bu_4NPF_6/DMF.

$DBSQ)]^{2-}$, respectively (Figs. 2 and 3). However, whereas the former species is the only product of the reaction between $Co(mnt)_2^{2-}$ and o-DBQ, the free o-DBSQ radical-anion is formed together with the $[Co(pfmdt)_2(o\text{-}DBSQ)]^{2-}$ complex (Fig. 3). On the other hand, the reaction between $Co(tdt)_2^{2-}$ and o-DBQ produces only separated electron-transfer products, *i.e.*, $Co(tdt)_2^-$ and free o-DBSQ, as was proven both spectroscopically (typical intense narrow absorption band of $Co(tdt)_2^-$ at 658 nm [25]) and by ESR which exhibits only strong doublet corresponding to free o-DBSQ.

The reactions between planar Co(II) complexes and o-DBQ mentioned above were also studied by absorption spectroscopy. In the case of Schiff-base and dithiolato complexes, only a small decrease in the absorption due to parent Co(II) complexes was observed upon the addition of a two-fold or larger molar excess of o-DBQ. On the other hand, the formation of the adduct of $Co(sacsac)_2$ with o-DBQ is essentially completed* under these conditions. However, weak absorption due to Co-

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*An intense absorption band at 311 nm and a weak one at 540 nm correspond to the $[Co(sacsac)_2(o\text{-}DBSQ)]$ complex

$(sacsac)_2$ is still seen when the complex and o-DBQ are in equimolar concentrations.

Apparently, the o-DBSQ radical adducts of planar Co(II) complexes (denoted generally Co^{II}(L)) are formed by a reversible oxidative addition:

$$Co^{II}(L) + o\text{-}DBQ \rightleftharpoons [Co^{III}(L)(o\text{-}DBSQ)] \qquad (1)$$

This equilibrium is shifted largely to the left for all studied Co(L) complexes except $Co(sacsac)_2$. The absorption spectra of the reaction mixture allow us to establish a qualitative dependence of the equilibrium constant on the nature of the equatorial ligand(s) L: sacsac > acacen ~ salen ≫ mnt ~ pfmdt.

When strongly oxidizing o-CQ ($E_{1/2} = +0.17$ V) is used instead of o-DBQ ($E_{1/2} = -0.47$ V), the formation of the radical-adduct is observed only in the case of Co(Schiff base) complexes in toluene. The [Co-(acacen)(o-CSQ)] species was characterized by ESR (Table I). The $Co(sacsac)_2$ complex reacts with o-CQ producing a pink, ESR-inactive solution which was not studied further. All three dithiolato complexes, *i.e.*, $Co(mnt)_2^{2-}$, $Co(pfmdt)_2^{2-}$ and $Co(tdt)_2^{2-}$, undergo one-electron oxidation by o-CQ in DMF solution producing $[Co(mnt)_2]_2^{2-}$, $[Co(pfmdt)_2]_2^{2-}$ and $Co(tdt)_2^-$, respectively, as was proved by absorption spectroscopy. The presence of reduced o-CSQ radical-anion was confirmed by ESR. These redox products undergo some slow follow-up reactions. No evidence for radical-adduct formation between Co(II) dithiolates and o-CQ has been found.

No enhancement of the formation of o-DBQ radical-adducts with Co(Schiff-base) and $Co(sacsac)_2$ is observed in the presence of coordinating solvents. The $[Co(sacsac)_2(o\text{-}DBSQ)]$ complex is formed in THF, DMF or in 5 M pyridine/toluene in concentrations which are comparable to those found in pure toluene. However, its decomposition is much faster; the rate of this process decreases in the order: 5 M pyridine/toluene > DMF > THF ≫ pure toluene. This decay of the $[Co(sacsac)_2(o\text{-}DBSQ)]$ radical-adduct cannot be simply explained by a substitution of o-DBSQ ligand by solvent molecules because no ESR-active species are formed.

In the case of the Co(acacen) complex, the formation of radical-adduct with o-DBQ is even less pronounced in DMF or in THF than in toluene. Addition of pyridine in concentrations of 10^{-2}–10^{-1} M to the toluene solutions of Co(Schiff-base) complexes has no effect on the formation of their radical-adducts with o-DBQ. However, in 6 M pyridine/toluene or in neat pyridine, free o-DBSQ radical anion is formed in addition to the $[Co(Schiff-base)(o\text{-}DBSQ)]$ complexes. The ratio of the amplitudes of the ESR signals corresponding to the radical adducts and to free o-DBSQ is the same whether pyridine (6 M) is added to the solution of Co(Schiff-base) complex before its reaction with o-DBQ or after mixing the

reactants *i.e.*, to the toluene solution where an equilibrium concentration of the radical-adduct was already established. This experiment reflects the reversible nature of both quinone oxidative addition 1 and electron transfer producing free *o*-DBSQ radical. Moreover, when the reaction between Co-(acacen) and *o*-CQ is carried out in DMF instead of toluene, free *o*-CSQ is the main reaction product as is reflected by ESR. The radical-adduct [Co(acacen)-(*o*-CSQ)] is also formed, although only in a very small concentration.

All *para*-quinones used in this study, *i.e.*, *p*-CQ, *p*-BQ and *p*-DBQ, were found to be completely unreactive toward Co(sacsac)₂ and both Co(Schiff-base) complexes in toluene. However, Co(acacen) is fully oxidized by *p*-CQ in DMF and by *p*-BQ in neat pyridine. A small equilibrium concentration of free *p*-DBSQ was detected by ESR in pyridine solution containing Co(acacen) and *p*-DBQ. Free *p*-CSQ and *p*-BSQ are formed in low concentrations by the reaction of Co(salen) with *p*-CQ or *p*-BQ in DMF or pyridine, respectively. No reaction takes place between Co(salen) and *p*-DBQ in any of the studied solvents.

The Co(mnt)₂²⁻ is stoichiometrically oxidized in DMF or THF by *p*-CQ to [Co(mnt)₂]₂²⁻. No reaction takes place between Co(mnt)₂²⁻ and either *p*-BQ or *p*-DBQ. The Co(pfmdt)₂²⁻ complex does not react with *p*-DBQ, whereas the Co(tdt)₂²⁻ is readily oxidized to Co(tdt)₂⁻. The formation of oxidized dithiolates in these reactions was proved by absorption spectra, whereas *p*-semiquinone radicals were detected by ESR.

No evidence for the formation of radical-adducts between any of studied planar Co(II) complexes and *para*-quinones has been found.

Discussion

The reactions of planar Co(II) complexes described above produce some new *o*-semiquinone complexes of Co(III), *i.e.*, [Co(sacsac)₂(*o*-DBSQ)], [Co(mnt)₂(*o*-DBSQ)]²⁻, [Co(pfmdt)₂(*o*-DBSQ)]²⁻ and [Co(acacen)(*o*-CSQ)]. The [Co(acacen)(*o*-DBSQ)] and [Co(salen)(*o*-DBSQ)] have been, on the other hand, previously prepared in the solid state [15, 16]. Information on analogous [Co(salophen)(*o*-semiquinone)] [17, 18], [Co(trien)(*o*-DBSQ)] [27] and *p*-, *o*-DBSQ radical-adducts with Co(CN)₅³⁻ [3, 4] is also available in the literature. Comparison of the relevant ESR parameters (Table I) shows that all the newly described compounds exhibit similar ESR features typical for complexes containing one *o*-semiquinone radical-anion ligand bound to a diamagnetic central metal atom [3, 4, 9, 11, 13, 15–18, 31–35], in full agreement with their formulation as Co(III) complexes. The a_H value

(corresponding to C(4)-bonded H-atom of the quinone [33, 34]) is equal to or slightly larger than that of free *o*-DBSQ; the cobalt splitting constants are significantly larger than those of the [Co(CN)₅-(*o*-DBSQ)]³⁻ and [Co(CN)₅(*p*-DBSQ)]³⁻ species containing monodentate *ortho*- and *para*-DBSQ, respectively. The a_{Co} value is, however, comparable to that of the [Co(CN)₄(*o*-DBSQ)]³⁻ complex containing chelated *o*-DBSQ [4]. This shows that some π-delocalization is present in the planar {Co^III-(*o*-semiquinone)} chelate ring. The *g*-values are typically lower than those of free *o*-DBSQ, except for the dithiolato complexes, especially the pfmdt complex. Larger electron density on the Co-central atom due to dithiolato ligands and resulting weak cobalt–semiquinone bonding may account [35] for this effect.

Two kinds of reactions were found to take place between planar complexes and quinones:

1. Reversible oxidative addition

$$Co^{II}(L) + o\text{-}Q \rightleftharpoons Co^{III}(o\text{-}SQ)(L) \qquad (I)$$
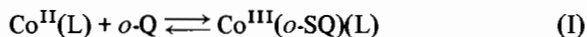
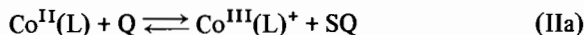L = sacsac₂; Q = *o*-DBQ; in toluene, DMF, THF, 6 M py/toluene

L = acacen, salen; Q = *o*-DBQ; in toluene, DMF, THF, 6 M py/toluene

L = acacen; Q = *o*-CQ; in toluene, DMF

L = mnt₂, pfmdt₂; Q = *o*-DBQ; in DMF, THF

No coordination of solvent molecule prior to the oxidative addition takes place.

2. Electron transfer

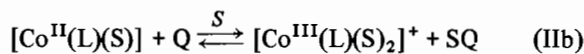$$Co^{II}(L) + Q \rightleftharpoons Co^{III}(L)^+ + SQ \qquad (IIa)$$

(Note that SQ is a radical-anion, (Q⁻))

L = mnt₂ Q = *o*, *p*-CQ; in DMF, THF

L = pfmdt₂; Q = *o*-DBQ, *o*, *p*-CQ; in DMF, THF

L = tdt₂; Q = *o*, *p*-DBQ, *o*, *p*-CQ; in DMF, THF

$$[Co^{II}(L)(S)] + Q \overset{S}{\rightleftharpoons} [Co^{III}(L)(S)_2]^+ + SQ \qquad (IIb)$$

L = acacen; Q = *o*,*p*-CQ; in DMF

Q = *o*-DBQ; in 6 M py/toluene

Q = *p*-BQ, *p*-DBQ; in neat py

L = salen; Q = *p*-CQ; in DMF

Q = *p*-BQ; in neat py

Coordination of the solvent molecule, S, prior to the electron transfer is necessary in the case of IIb-type reactions.

The electron transfer reaction is thermodynamically quite unfavorable for most of the reactions listed under the oxidative addition pathway (I), as can be seen by the comparison of the values of corresponding redox potentials (Table II). However, when the nature of either the ligand or quinone or solvent is changed in such a way that the electron transfer (II) becomes thermodynamically competitive, both radical adduct and separated redox products are

TABLE II. Oxidation Potentials of Square Planar Co(II) Complexes and Reduction Potentials of Quinones[a]

Compound	$E_{1/2}$	Solvent	Note
$Co(mnt)_2^{2-}$	+0.16	DMF	b, c
$Co(pfmdt)_2^{2-}$	−0.19	DMF	c
$Co(tdt)_2^{2-}$	−0.88	DMF	d
$Co(sacsac)_2$	> +0.5	DMF	e
$Co(acacen)_2$	+0.015	DMF	f
$Co(acacen)_2$	−0.35	6×10^{-1} M py/DMF	f
$Co(acacen)_2$	−0.49	py	f
$Co(salen)_2$	+0.225	DMF	f
$Co(salen)_2$	−0.28	6×10^{-1} M py/DMF	f
$Co(salen)_2$	−0.31	py	f
o-DBQ	−0.47	DMF	g
o-CQ	+0.17	DMF	g
p-DBQ	−0.60	DMF	g
p-CQ	+0.09	DMF	g
p-BQ	−0.42	DMF	g

[a]$E_{1/2}$ values in volts, determined vs. Ag/AgCl reference electrode. Mercury dropping electrode was used. All redox couples are electrochemically reversible, i.e. $E_{1/2} \cong E^o$. [b]Rotating Pt electrode. [c]Refers to Co^{II}/Co_2^{III} couple (see text). [d]Co^{II}/Co^{III} couple. [e]Not oxidizable at DME. [f]Refers to Co^{II}(Schiff-base)/[Co^{III}(Schiff-base)-S_2]$^+$ couple. [g]Refers to Q/SQ couple.

observed simultaneously, as is the case in the reaction between $Co(pfmdt)_2^{2-}$ and o-DBQ or between both studied Co(Schiff-base) complexes and o-DBQ in 6 M py/toluene. No radical adduct formation is observed when the electron transfer path (II) is thermodynamically greatly favoured (The oxidation of $Co(dithiolene)_2^{2-}$ complexes by o-CQ or the reaction between $Co(tdt)_2^{2-}$ and o-DBQ fall into this category.) All these observations point to the conclusion that both oxidative addition and electron transfer between planar Co^{II}(L) complexes and ortho-quinones are equally possible kinetically, the corresponding equilibria (I) and (II) being established rapidly**. The nature of the observed reaction product is then determined by the overall thermodynamics, i.e., by the values of the redox potentials of the reacting species in given media and by the bonding energy of the {Co^{III}(o-semiquinone)} chelate ring. On the other hand, the oxidative addition of para-quinones to planar Co^{II}(L) species is obviously unfavorable kinetically.

As was mentioned in the introduction, the orbital matching scheme explaining the oxidative addition of quinones to a square pyramidal $Co^{II}(CN)_5^{3-}$ complex

cannot be applied, for symmetry reasons, to the analogous reactions of planar Co^{II}(L) complexes possessing the d_{yz}^1 electron configuration [19, 40, 41]. Indeed, the difference in the intimate reaction mechanism involved in the reactions of quinones with these two types of Co^{II} complexes is reflected in the experimentally observed behavior. (i) Whereas both ortho- and para-quinone isomers add oxidatively to $Co(CN)_5^{3-}$ [3, 4], no oxidative addition of para-quinones to the Co^{II}(L) species was observed at all. (ii) No intermediate containing a monodentate o-DBSQ ligand bound to the Co^{III} central atom by only one oxygen atom was found to be involved in the oxidative addition of o-DBQ to Co^{II}(L), contrary to the analogous reaction of $Co(CN)_5^{3-}$ [4].

The observed oxidative additions of o-quinones to planar Co^{II} complexes may be explained by simultaneous interaction between both quinone oxygen atoms and the Co^{II} central atom in the transition state. The quinone molecule is assumed to approach the planar Co(L) molecule perpendicularly, in such a way that one oxygen atom interacts with the Co^{II} atom axially, i.e., in the direction of the z-axis. The π^* (LUMO) orbital of the quinone overlaps (through its 2p-oxygen component) with the singly occupied d_{yz} cobalt orbital, opening the path for the electron transfer. Due to its lone electron pair, this oxygen atom behaves also as a Lewis base, and Co—O σ-bond is simultaneously created. The second oxygen atom of the quinone molecule is sterically determined to push, at the same time, one of the equatorial donor atoms below the Co(L) molecular plane, forming concomitantly the second Co—O σ-bond. The simultaneous electron transfer, formation of two cobalt—oxygen bonds and rearrangement of the equatorial ligand system to the final pseudo-octahedral geometry leads in a concerted manner to the formation of the {Co^{III}(o-semiquinone)} chelate ring. The aforementioned absence of an intermediate containing a monodentate o-DBSQ ligand and the unreactivity of p-quinones via the oxidative addition pathway (I) are in full agreement with the concerted mechanism of the oxidative addition described above.

The addition of a coordinating solvent, such as pyridine, usually promotes the d_{z^2} orbital in the Co^{II}(L) complexes achieving the $d_{z^2}^1$ configuration [19, 29, 40]. The Co^{II}(Schiff-base) complexes can, in this way, be made reactive toward substrates like organic halides or O_2 [42], which then add oxidatively. However, this effect was not observed either in the case of the reaction with ortho- or with para-quinones. Instead, the decrease of the oxidation potential of the Co^{II}(L) complex by the coordination of the solvent molecule [20, 42] opens the electron transfer pathway IIb, and the quinones are simply reduced to free semiquinone radical-anions by the Co^{II}(Schiff-base) complexes in strongly coordinating solvents.

**It was reported [16] that the formation of [Co(salen)(o-DBSQ)] is very slow. However, the reversibility of the reaction between Co(salen) and o-DBQ was not recognized. In fact, the rate of the synthesis of this complex is determined by the rate of its precipitation from the THF solution shifting the equilibrium (1) to the right. The time needed to synthesize [M(salen)(o-DBSQ)]; M = Mn, Fe, Co [16]; is thus not related to the rate of the oxidative addition.

The oxidative addition (I) may take place only if the bonding energy of the {Co^{III}(*o*-semiquinone)} chelate ring is sufficient to compensate for the energetically unfavorable oxidation of Co^{II} connected with the rearrangement of the equatorial ligands and with the loss of the π-delocalization of the original planar system. Indeed, the observed dependence of the extent of the radical-adduct formation in the equilibrium (I) on the nature of the equatorial ligand L, *i.e.*, sacsac > Schiff-base ≫ dithiolates, decreases in the same order as the π-delocalization in the parent Co^{II}(L) complexes increases [19, 26, 36–41].

The high extent of π-delocalization in Co^{II}(dithiolato)$_2$$^{2-}$ complexes [26, 30, 36–39, 41] has been recently employed [36] to explain apparent unreactivity of these complexes by the oxidative addition mechanism. Noteworthy, the described reactions between Co(mnt)$_2$$^{2-}$ or Co(pfmdt)$_2$$^{2-}$ with *o*-DBQ represent, to our knowledge, the first known example of the oxidative addition to dithiolato complexes of cobalt(II). The unique ability of *o*-DBQ to form stable [11] {M(*o*-DBSQ)} chelate rings in a single reaction step (see above) makes the otherwise unfavorable oxidative addition to the Co^{II}(dithiolato)$_2$$^{2-}$ complexes possible.

It is thus evident that the oxidative addition of quinones to transition metal complexes may take place by various mechanisms. The actual reaction path is very sensitive to any changes in the structure of the metal complex, for example, loss of strong axial interaction going from Co(CN)$_5$$^{3-}$ complex to Co(L) species completely changes the mechanism. The competition between simple electron transfer and oxidative addition must also be taken into account as an important factor in the quinone–metal complex reactivity.

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