Inorganica Chimica Acta, 69 (1983) 191–197

The Parallelism in the Mechanisms of the One-Electron Oxidative Additions of *ortho*- and *para*-Quinones to $Co(CN)_5^{3-}$

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Received May 27, 1982

Ortho- as well as para-quinones were found to add oxidatively to the typical metal-centered radical, $Co^{II}(CN)_5^{3-}$, producing in aprotic media radical adducts of Co^{III} with p-semiquinone or monodentate o-semiquinone radical ligands, respectively. The electronic structure and bonding is quite similar in the adducts of both o- and p-quinones as is reflected by EPR and UV-VIS spectra. These radical adducts are rather labile, releasing free semiquinone radicals. The adduct of monodentate o-semiquinone represents a novel structural type of o-semiquinone bonding. It undergoes a slow follow-up intramolecular substitution reaction, producing a complex with the bidentate o-semiquinone radical ligand chelated to Co^{III}.

Introduction

One-electron redox reactions of quinones with transition metal complexes are of great importance in many biological and catalytical processes [1], *e.g.* in respiratory chains and photosynthesis [1–5]. They also represent an excellent model for testing various theories of redox reactivity. Reactions of *o*-quinones with low-valent transition metal complexes are regarded as a unique class of oxidative additions [6] occurring as two- or one-electron processes producing catecholate [6–9] or *o*-semiquinone [10–15] radical complexes, respectively. These compounds often possess quite unusual bonding and structural properties and they might also have biological and catalytical importance [1].

The majority of the experimental work in the field of metal–quinone chemistry has so far been concerned with the determination of molecular structure of these compounds [1] without any relations to the intrinsic mechanism of their formation.

Recently, we described [16] a novel species $[Co(CN)_5(p\text{-DBSQ})]^{3-}$ containing 2,6-di-tert-butyl-*p*-benzosemiquinone radical coordinated to Co^{III} central atom, formed *via* an oxidative addition of corresponding *p*-quinone to $Co(CN)_5^{3-}$. This typical metal-centered radical appeared to be a very suitable model compound for following the one-electron oxidative additions [16].

The present systematic study of the reactions of various *ortho*- as well as *para*-quinones has been performed with the aim of obtaining more insight into the problem of quinone one-electron oxidative additions, and to make a comparison between the intrinsic mechanisms of the oxidative additions of *ortho*- and *para*-quinones.

Experimental

Chemicals

Anhydrous $CoCl_2$ was prepared from $CoCl_2 \cdot 6H_2O$ by refluxing with 2,2′-dimethoxypropanol. Bu_4NCN was prepared according to Solodar [17]. N,N′-dimethylformamide (DMF), Merck, was purified by distillation with benzene under argon atmosphere. The following quinones were used: 2,3,5,6-tetrachloro-1,4-benzoquinone (Lachema Brno) was recrystallized from benzene, *p*-benzoquinone (Lachema Brno) was resublimed; 2,6-di-tert-butyl-1,4-benzoquinone and 2,3,5,6-tetramethyl-1,4-benzoquinone (duroquinone) were used as obtained from the Aldrich Chemical Company, Inc.; 3,4,5,6-tetrachloro-1,2-benzoquinone, 9,10-phenanthrenequinone, (Fluka) were used without further purification; 3,5-di-tert-butyl-1,2-benzoquinone and 1,2-naphtoquinone were used as obtained from EGA Chemie.

Instrumentation

EPR measurements were performed with a Varian E4 X-band spectrometer. Electronic spectra were obtained with a Unicam SP 800B spectrophotometer.

Experimental Conditions

Solutions of $Co(CN)_5^{3-}$ in DMF were prepared by dissolution of appropriate amounts of $CoCl_2$ and Bu_4NCN in DMF ([CN]/[Co] = 5.5–7). Very

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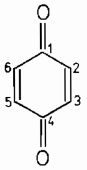
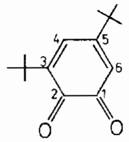
air-sensitive, light-yellow solutions were formed; they were handled in closed apparatus under pure argon atmosphere or under vacuum. All reactions were performed at low temperature (–60 °C). The cells for EPR and spectral measurements were filled under vacuum and sealed off. The measurements of both kinds of spectra were performed at 0 °C, 2–3 minutes after mixing of the reactants.

Results

The reactions of:
2,3,5,6-tetrachloro-1,4-benzoquinone (p-CQ)
1,4-benzoquinone (p-BQ, see (I))
2,6-di-tert-butyl-1,4-benzoquinone (p-DBQ)
2,3,5,6-tetramethyl-1,4-benzoquinone (duroquinone, DuQ)
3,4,5,6-tetrachloro-1,2-benzoquinone (o-CQ)
3,5-di-tert-butyl-1,2-benzoquinone (o-DBQ, see (II))
1,2-naphtoquinone (NQ)
9,10-phenanthrenequinone (PQ)
with Co(CN)$_5^{3-}$ were performed by addition of a stoichiometric amount of quinone dissolved in DMF to the solution of Co(CN)$_5^{3-}$ at –60 °C. The experimental conditions used ensured that the actually reacting Co^{II} species was the Co(CN)$_5^{3-}$ complex [16].



I



II

All reactions studied occurred immediately when the reactants were mixed together, producing intensively coloured solutions: p-CQ; p-BQ; p-DBQ; o-CQ-orange; DuQ-red-orange; o-DBQ-blue; NQ-violet; PQ-wine-red. EPR spectra of these solutions show disappearance of the broad signal [16] of Co(CN)$_5^{3-}$ and prove the formation of a new radical species. In the case of p-CQ, o-CQ, NQ and PQ, free semiquinone (SQ) radicals only were detected as final reaction products, whereas p-DBQ, p-BQ and o-DBQ were unequivocally proved to produce radical adducts with Co(CN)$_5^{3-}$. Duroquinone was found to form only a minute concentration of a radical adduct whose poorly resolved EPR spectrum very rapidly disappeared, thus preventing further characterization. Free durosemiquinone radical was produced as a final reaction product.

Only reactions of p-DBQ, p-BQ and especially of o-DBQ with Co(CN)$_5^{3-}$ were thus subjected to further experimental study.

Both p- and o-quinones were also found to react with free CN$^-$-ions, the former producing SQ-radicals and the latter reacting with CN$^-$ very slowly under formation of EPR-inactive products together with traces of free SQ-radicals. The reactions of p-quinones with CN$^-$ ions do not occur rapidly, the reaction rate decreases in the order p-CQ > p-BQ > p-DBQ > DuQ. In the case of p-CQ and p-BQ some other unidentified radical species were formed in addition to the corresponding SQ radicals. These by-products were never observed after the reaction of these quinones with Co(CN)$_5^{3-}$. The reaction of quinones with CN$^-$ may be thus supposed [16] to be too slow to interfere with their reactions with Co(CN)$_5^{3-}$, which are very fast even at low temperatures.

Reaction with 2,6-di-tert-butyl-p-benzoquinone (p-DBQ)

This reaction and its product [Co(CN)$_5$(p-DBSQ)]$^{3-}$ was described recently [16] as one-electron oxidative addition of quinone producing a complex of p-semiquinone (p-DBSQ) radical ligated to Co^{III} central atom *via* the oxygen donor atom. For EPR-parameters, see Table I. This complex rapidly decomposes liberating free p-DBSQ radical [16].

Reaction with p-benzoquinone (p-BQ, (I))

When a stoichiometric amount of p-BQ dissolved in DMF was added to the solution of Co(CN)$_5^{3-}$ at –60 °C, the colour immediately turned to orange, and the EPR spectrum measured at 0 °C (Fig. 1, curve a) exhibits a complicated signal attributed to the radical adduct with Co(CN)$_5^{3-}$ partially overlapped by a typical five-line signal of free p-benzosemiquinone radical (p-BSQ). Upon standing at 0 °C or higher temperature, the colour turns rapidly to yellow, the EPR signal of the adduct disappears and that of free p-BSQ radical increases in intensity. The EPR signal of the adduct was interpreted as that of p-BSQ radical splitted by the interaction with the ^{59}Co (I = 7/2) central atom, proving the existence of a direct p-BSQ–cobalt bond. Moreover, the splitting due to two different groups of two ^{1}H atoms is observed in the EPR spectrum. The original symmetry equivalence of all four ^{1}H atoms of the p-BSQ radical is thus destroyed by the coordination and the unequivalence between the two groups of ^{1}H atoms bonded at C$_2$, C$_6$ and C$_3$, C$_5$ positions (see (I) for the numbering) proves that the p-BSQ radical is bound to the Co atom assymetrically via one oxygen atom, and the local symmetry of the semiquinone is decreased from D$_{2h}$ to C$_{2v}$ point group. The symmetrical η^4-coordination of the quinone moiety to the Co-atom (see *e.g.* 25, 26) is thus excluded*.

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*The η^4-coordination was also excluded in the case of p-DBSQ adduct based on electrochemical arguments [16].

TABLE I. EPR Spectra of Selected Semiquinone Complexes.

Coumpound	g-factor	a_{Co}[a]	a_H[a]	Ref.
o-DBSQ	2.0047	–	0.315	this work
$[Co(CN)_5(o\text{-}DBSQ)]^{3-}$, (III)	2.0044	0.257	0.228	this work
$[Co(CN)_4(o\text{-}DBSQ)]^{2-}$, (IV)	2.0026	0.89	0.31	this work
[Co-bae(o-DBSQ)][b]	2.0019	1.12	0.36	x[d]
$[Co\text{-}trien(o\text{-}DBSQ)]^{2+}$[c]	–	0.976	0.35	22
[Co-salen(o-DBSQ)][e]	2.00	1.02	0.35	11
$[Re(CO)_4(o\text{-}DBSQ)]$	2.003	–	0.346	12
p-BSQ	2.0052	–	0.241	this work
$[Co(CN)_5(p\text{-}BSQ)]^{3-}$	2.0052	0.252	0.165 (C_3, C_5) 0.304 (C_2, C_6)	this work
$Ph_3Ge{\bullet}p\text{-}BSQ$	–	–	0.088 (C_3, C_5) 0.585 (C_2, C_6)	23
p-DBSQ	2.0052	–	0.214	16
$[Co(CN)_5(p\text{-}DBSQ)]^{3-}$	2.0050	0.244	0.140	16

[a] a_H, a_{Co} values in mT. [b] bae = bis(acetylacetone)ethylenediimine dianion. [c] trien = triethylenetetramine. [d] x = see ref. 13, given values of g-factor, a_H, a_{Co} in DMF: this work. [e] salen = N,N′-ethylenebis(salicylidenimine) dianion.

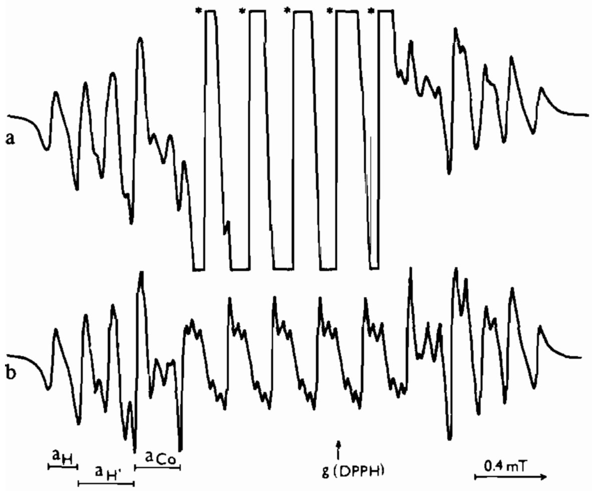


Fig. 1. EPR spectrum of $[Co(CN)_5(p\text{-}BSQ)]^{3-}$. $4{,}9.10^{-3}$ mol l^{-1} of p-BQ added to 5.10^{-3} mol l^{-1} $CoCl_2$, 3.10^{-2} mol l^{-1} Bu_4NCN in DMF at –60 °C. Measured at 0 °C. *: signals of free p-BSQ, a: experimental, b: computer simulated spectrum.

The EPR spectrum obtained may be thus attributed to a $[Co(CN)_5(p\text{-}BSQ)]^{3-}$ species containing p-BSQ radical bonded to the Co^{III} central metal atom *via* oxygen donor atom.

Corresponding EPR parameters may be obtained from the experimental EPR spectrum with sufficient accuracy; nevertheless we performed the computer-simulation of the spectrum to confirm the assignment of the hyperfine splitting outlined above. The computed spectrum (Fig. 1, curve b) is in a very good agreement with the experimental one. Corresponding EPR parameters are collected in Table I. These parameters are comparable with those of the $[Co(CN)_5(p\text{-}DBSQ)]^{3-}$ complex (Table I, ref. 16), as well as with those of p-BSQ adducts of non-transition metals [23]. The assignment of a_H constants to the H(2,6) and H(3,5) groups of hydrogen atoms was made by comparison with the $[Co(CN)_5(p\text{-}DBSQ)]^{3-}$ complex where only the H(3,5) group of ^1H atoms is available, provided that in complexes of both p-BSQ and p-DBSQ the semiquinone ligand is linked to the Co atom *via* the C_4-oxygen donor atom.

The electronic absorbtion spectrum of the $[Co(CN)_5(p\text{-}BSQ)]^{3-}$ radical adduct is very similar to that of free p-BSQ (Fig. 2). The radical adduct is characterized by the shoulder at 500 nm which rapidly disappears producing the characteristic spectrum of free p-BSQ radical (Fig. 2, dashed line). Other visible spectral bands of the radical adduct almost coincide with those of free p-BSQ radical, as well as the UV band at approx. 318 nm (free p-BSQ: 325 nm). Analogous p-DBSQ radical adducts exhibit identical spectral behaviour [16]. However, the detailed description of the absorbtion spectrum of the adduct is complicated by overlap with that of free p-BSQ radical, which is always present due to great instability of the radical adduct.

The observed EPR and electronic spectra of the product of the reaction of $Co(CN)_5^{3-}$ with p-BQ are fully consistent with those expected for *$[Co(CN)_5(p\text{-}BSQ)]^{3-}$ complex containing p-BSQ radical ligand bound to the Co^{III} central metal.* Comparison with the recently characterized $[Co(CN)_5(p\text{-}DBSQ)]^{3-}$ complex [16] supports this conclusion.

The $[Co(CN)_5(p\text{-}BSQ)]^{3-}$ complex rapidly decomposes in solution liberating free p-BSQ radicals, as was proved by EPR and visible spectra. This decomposition is faster than that of the corresponding p-DBSQ complex [16].

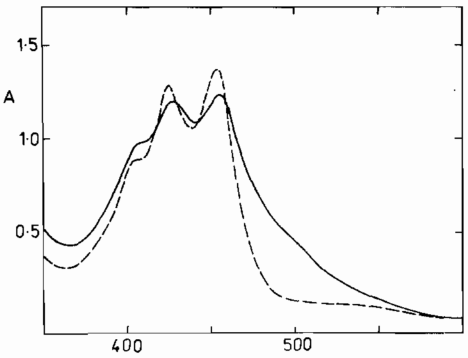


Fig. 2. Absorbtion spectrum of $[Co(CN)_5(p\text{-}BSQ)]^{3-}$ (full line) and of its decomposition product p-BSQ (dashed line). $1{,}6 \times 10^{-4}$ mol l^{-1} of p-BQ added to $1{,}6 \times 10^{-4}$ mol l^{-1} $CoCl_2$ and $1{,}2 \times 10^{-3}$ mol l^{-1} Bu_4NCN in DMF at −60 °C. Spectrum measured at 0 °C. Dashed line after 2 hrs at +20 °C.

The free p-BSQ radical was also found to be the final reaction product when sub-stoichiometric amounts of p-BQ were added to the solution of $Co(CN)_5^{3-}$ ([Co]/[BQ] = 3–4): EPR signals due to both residual $Co(CN)_5^{3-}$ and free p-BSQ were observed. The formation of a dimeric species $[Co(CN)_5(\mu\text{-}OC_6H_4O)Co(CN)_5]^{6-}$, which is of crucial importance in water [18–20], is thus of no significance in the aprotic media.

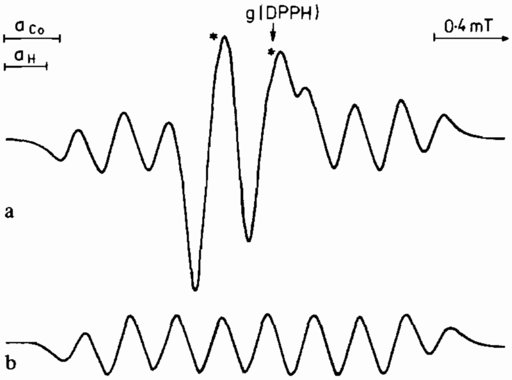
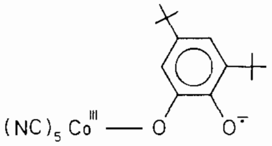


Fig. 3. EPR spectrum of $[Co(CN)_5(o\text{-}DBSQ)]^{3-}$, (III). $5{,}05 \times 10^{-3}$ mol l^{-1} of o-DBQ added to $5{,}05 \times 10^{-3}$ mol l^{-1} $CoCl_2$ and $3{,}2 \times 10^{-2}$ mol l^{-1} Bu_4NCN in DMF at −60 °C. Spectrum measured at 0 °C. a: experimental, b: computer-simulated spectrum. *: signal of free o-DBSQ.

Reaction with 3,5-di-tert-butyl-o-quinone (o-DBQ, II)

When the stoichiometric amount of o-DBQ in DMF was added to the solution of $Co(CN)_5^{3-}$ at −60 °C, the colour immediately turns to deep blue. In the EPR spectrum (Fig. 3, curve a) the signal of $Co(CN)_5^{3-}$ disappears and a new, nine-line signal partially overlapped with that of free 3,5-di-tert-butyl-o-benzosemiquinone radical (o-DBSQ) appears. This nine-line signal rapidly decreases at 0 °C or at higher temperatures whereas that of the free o-DBSQ radical simultaneously increases*. No other radical species is formed under these conditions. These results may be interpreted as a formation of cobalt-o-DBSQ adduct by the reaction of o-DBQ with $Co(CN)_5^{3-}$, which further decomposes liberating free o-DBSQ radical. However, the nine-line EPR spectrum is quite unusual in the metal-o-semiquinone chemistry [1, 10–14]. The observed hyperfine splitting may be attributed to the ^{59}Co (I = 7/2) nucleus and to one ^1H atom of the o-semiquinone ligand (presumably C_4-hydrogen, see ref. 21, 24). This EPR spectrum was computer-simulated with excellent agreement (Fig. 3, curve b). Hyperfine splitting constants obtained do not fall into the range typical for complexes with chelated o-semiquinone radical ligands [10–14, 21, 22, 24], which are characterized by a g-factor much lower than that of free o-DBSQ radical, a_H constant equal or larger than that of free o-DBSQ and a_{Co} constant of about 1 mT (see Table I for some typical complexes and for free o-DBSQ radical). Complexes containing chelated o-DBSQ ligand are also more substitutionally stable than the new species observed [11–13, 22]. In fact, the EPR parameters found are quite similar to those of the corresponding p-semiquinone complex $[Co(CN)_5(p\text{-}DBSQ)]^{3-}$ [16]. Based on this analogy, we attributed the observed nine-line EPR spectrum to the complex containing *novel bonding type of o-semiquinone ligand, i.e. monodentate o-DBSQ radical ligand linked to the* Co^{III} *central atom via* C_1*-oxygen atom only. This complex may be thus formulated as* $[Co^{III}(CN)_5(o\text{-}DBSQ)]^{3-}$*, (III).*



III

When the decomposition of this complex is suppressed by low temperature (−60 °C) for more than 30 minutes, a new EPR signal composed of eight triplets may be detected in addition to the signal of free o-DBSQ radical and that of remaining species (III). When low total concentration of the reactants is used (about 3.10^{-4} mol l^{-1}) and the temperature is very slowly (during 2 hours) increased from −60 °C to +20 °C this eight-triplet spectrum (Fig. 4), partially overlapped with that of free o-DBSQ radical, may be obtained without any signals due to remaining species (III) which was decomposed during the slow temperature increase. This spectrum (Fig. 4)

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*After prolonged standing of the solution, the intensity of the free o-DBSQ EPR signal starts slowly to decrease.

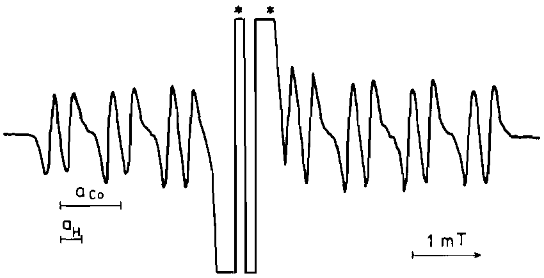
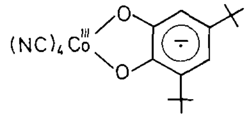


Fig. 4. EPR spectrum of $[Co(CN)_4(o\text{-}DBSQ)]^{2-}$, (IV). 2.84×10^{-4} mol l^{-1} of o-DBQ added to 3.10^{-4} mol l^{-1} $CoCl_2$ and 2.10^{-3} ml l^{-1} Bu_4NCN at −60 °C. Spectrum measured at +20 °C after 2 hrs. *: signals of free o-DBSQ.

may be directly attributed to the *Co^{III} complex containing chelated bidentate o-DBSQ radical ligand* as its shape as well as the EPR parameters are quite comparable with those of other complexes of chelated o-semiquinones [10–14, 21, 22, 24]. This final product of the reaction of o-DBQ with $Co(CN)_5^{3-}$ may be described as a *$[Co^{III}(CN)_4(o\text{-}DBSQ)]^{2-}$ complex (IV).* This compound is fairly stable in the DMF solution, even in air.



IV

The reaction of o-DBQ with $Co(CN)_5^{3-}$ was also followed by electronic absorbtion spectroscopy (Fig. 5). Interpretation of the spectra is complicated by overlap with those of the free o-DBSQ radical. However, it may be stated that the spectrum of (III) (Fig. 5, curve 1) is very similar to that of free o-DBSQ radical (curves 2–6, Fig. 5). The corresponding maximum (λ = 665 nm) is only slightly blue-shifted with respect to that of o-DBSQ radical (λ = 670 nm). The extinction coefficient of (III) ($\epsilon \geqslant 960$) is slightly greater than that of the free o-DBSQ ($\epsilon \doteq 750$). The spectrum of (III) changes very rapidly into that of free o-DBSQ, whose absorbtion peak slowly decreases below the value corresponding to free o-DBSQ, in accordance with the EPR results. No spectral changes were observed in the UV region, except for a decrease of the absorbance. The spectrum of (IV) could not be measured due to high excess of free o-DBSQ radical.

The results obtained by EPR and UV-VIS spectra are consistent with the following mechanism:

Primarily the species (III) is formed very rapidly. This compound, containing a monodentate o-semiquinone ligand, decomposes rather rapidly, releasing free o-semiquinone radical. In a parallel much slower process the species (IV) is formed, containing the o-semiquinone bound as a bidentate ligand.

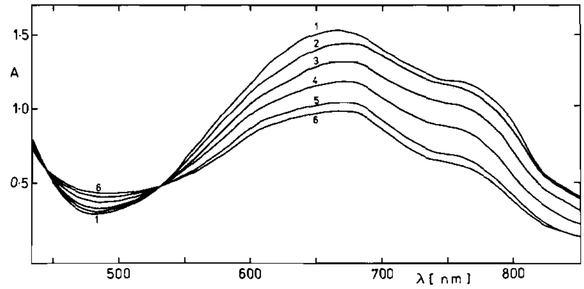


Fig. 5. Absorbtion spectrum of $[Co(CN)_5(o\text{-}DBSQ)]^{3-}$ and of its decompositon products. $1{,}6 \times 10^{-3}$ mol l^{-1} of o-DBQ added to $1{,}6 \times 10^{-3}$ mol l^{-1} $CoCl_2$ and $9{,}4 \times 10^{-3}$ Bu_4NCN at −60 °C. Spectra measured at 0 °C. Time: 1: 160 s, 2: 280 s, 3: 16 min., 4: 36 min., 5: 81 min., 6: 126 min. after mixing of the reactants. Curve 5 and further T = +20 °C.

Discussion

The primary step of the reaction of *ortho-* and *para*-quinones (Q) with $Co(CN)_5^{3-}$ is *identical* and may be represented by following reaction:

$$Co^{II}(CN)_5^{3-} + Q \xrightarrow{\text{v.fast}} [Co^{III}(CN)_5(SQ)]^{3-} \qquad (1)$$

The reaction (1) represents the one-electron oxidative addition of quinone to $Co^{II}(CN)_5^{3-}$. The unpaired electron is completely transferred to the quinone, the resulting semiquinone radical is linked to the Co^{III} central metal atom via one oxygen atom in the case of both *ortho-* and *para*-quinones. These species of the formula $[Co(CN)_5(SQ)]^{3-}$ (SQ = p-semiquinone or monodentate o-semiquinone radical ligand) are characterized by electronic absorbtion spectra almost identical with those of uncomplexed radicals. Also the g-factors of these radical complexes are very similar to those of free radicals. It may be concluded that the differences between the orbital energies of π-MO levels of the p-semiquinone and monodentate o-semiquinone ligands are almost unaltered by the coordination. However the distribution of the spin density is changed by the complexation, as is manifested by the a_H values: The EPR spectra of the $[Co(CN)_5(p\text{-}BSQ)]^{3-}$ complex show significant decrease of the a_H values corresponding to C_3, C_5 position whereas those corresponding to C_2, C_6 position are increased with respect to free p-BSQ radical (Table I), provided that the p-BSQ radical is bonded to Co^{III} via C_4-oxygen. These results point to the conclusion that the unpaired electron is localized predominantly on that part of the p-SQ ligand which is far apart from the cobalt atom: namely on C_2, C_6, C_1 and partially on the C_1-oxygen. Similar trends of a_H values were observed in $[Co(CN)_5(p\text{-}DBSQ)]^{3-}$ species as well as in p-BSQ adducts with non-transition metals [16, 23]. Even monodentate *o*-semiquinone radical ligand (*o*-DBSQ) exhibits significant lowering of the a_H value. The parallelism in the spin density distribution between the *o*- and *p*-quinones observed in free SQ radicals [24] is thus retained, even in the monodentate SQ radical ligands. *The intimate description of quinone one-electron oxidative addition* [16] *may be therefore assumed to be valid for both ortho- and para-quinones*: The unpaired electron is transferred from the d_{z^2} orbital of square pyramidal $Co^{II}(CN)_5^{3-}$ to the π-system of the quinone *via* an interaction with the p_z orbital of one oxygen atom of the quinone[≠]. Concerted net one-electron transfer reduces the quinone, whose electronic structure is dramatically altered, the p_z orbital of the oxygen donor atom being shut out from the π-system and the quinone oxygen turns into 'phenolate-type' oxygen which acts as a simple σ-donor atom towards the Co^{III} central atom. The lack of any significant π-interaction between Co^{III} and SQ radical ligands is manifested by the extremely low values of the a_{Co} splitting constants (Table I, ref. 16).

$[Co(CN)_5(SQ)]^{3-}$ complexes are substitution-labile, reacting with other solution species and liberating free SQ radicals:

$$[Co(CN)_5(SQ)]^{3-} + X \rightarrow [Co(CN)_5X]^{n-} + SQ \quad (2)$$

$(X = DMF, Cl^-, CN^-; n = 2,3)$

The rate of this reaction decreases in the order: *p*-BSQ > *o*-DBSQ > *p*-DBSQ. The complexes of *o*-CQ; *p*-CQ; NQ; PQ and DuQ are by analogy assumed to react according to reaction (1) and to decompose *via* reaction (2) so rapidly that any direct observation of the radical adducts of the type $[Co(CN)_5(SQ)]^{3-}$, even at −60 °C, is lacking. The enhanced stability of the adducts of di-butylated *o*- and *p*-semiquinones relative to all other adducts studied is presumably due to a significant, positive inductive effect of the -Bu^t substituent which increases strongly the donor ability of the semiquinone ligands.

When the liberation of free *o*-SQ radical is suppressed by low temperature for sufficiently long time, a *very slow intramolecular substitution process* (eqn. 3) *occurs*:

$$\underset{(III)}{[Co^{III}(CN)_5(o\text{-DBSQ})]^{3-}} \rightarrow \underset{(IV)}{[Co^{III}(CN)_4(o\text{-DBSQ})]^{2-}} + CN^- \quad (3)$$

The resulting $[Co(CN)_4(o\text{-DBSQ})]^{2-}$ complex (IV) contains a stable chelate ring $Co^{III}(o\text{-DBSQ})$, the Co^{III} atom presumably lying in the plane of the quinone.

This structure is much more favourable for π-bonding than the monodentate one as is reflected by the increase of the a_{Co}-value and by the decrease of the g-factor (see Table I).

The intramolecular process (3) is very slow as it requires substitution of one CN^- ligand bonded relatively strongly to a substitution-inert Co^{III} metal center. It may be assumed that the two-step mechanism involving: (i) one-electron oxidative addition of *o*-quinone to low valent metal center *via* only one oxygen atom, and (ii), an intramolecular process producing a complex with chelated *o*-semiquinone radical ligand is quite general, step (ii) being much faster when substitutionally less inert central metals are involved (*e.g.* Mn, Re, UO_2-group; refs. 10, 12, 14), or when only intramolecular rearrangement of the coordination sphere is involved (as is the case of *o*-quinone oxidative addition to square-planar complexes, see *e.g.* refs. 6–9, 11, 13).

Conclusion

In general, it might be concluded that oxidative additions of *ortho*- and *para*-quinones need not be regarded as two distinct types of reactions, as the oxidative additions of both *o*- and *p*-quinones involve the identical type of interaction of only one quinone oxygen atom with the radical metal center. The nature of the changes in the quinone electronic structure induced by the oxidative addition process, as well as the character of metal-semiquinone bonding in the resulting complexes, are also the same in the case of both *o*- and *p*-quinones. There is no reason to suppose any type of 'two-center' oxidative addition involving simultaneous attack of both *o*-quinone oxygen atoms on the metal radical center. However, the complexes containing monodentate *o*-semiquinone radical ligands also possess a possibility to close the chelate ring via an intramolecular process subsequent to an oxidative addition.

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[≠] The plane of the quinone is assumed to be parallel to the $Co(CN)_4$ plane in the early reaction stages.

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