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Coordinated *p*-Benzosemiquinone Radical: Formation of [Co(CN)$_5$(2,6-di-Bu^t-1,4-semiquinone)]$^{3-}$ by One Electron Oxidative Addition

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The product of the reaction of Co(CN)$_5^{3-}$ with 2,6-di-Bu^t-1,4-benzoquinone (DTBQ) in N,N'-dimethylformamide was characterized by EPR, UV–VIS spectroscopy and polarography as a Co^{III} complex with coordinated DTBQ$^{\bar{\cdot}}$ semiquinone radical, [Co(CN)$_5$(DTBQ)]$^{3-}$. This compound undergoes subsequent substitution reaction releasing free DTBQ$^{\bar{\cdot}}$ radical. The studied reaction is a one electron oxidative addition. The structure of [Co(CN)$_5$-(DTBQ)]$^{3-}$ and the reaction mechanism are discussed.

Introduction

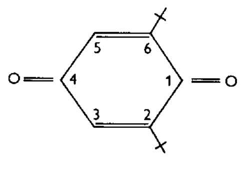
One-electron redox additions of transition metal complexes may be supposed to provide an effective mechanism for activation of various organic as well as inorganic substrates. Products of these reactions, *i.e.* coordinated radicals, may undergo further reaction steps in more selective and better controlled manner than analogous free radicals. Therefore one-electron redox additions are of great importance in homogeneous catalysis.

However, the factors influencing the reactivity of both substrates and transition metal-centered radicals are not completely understood. There are several problems, *e.g.* localisation of the unpaired electron after the redox process, concerted one-electron redox and coordination *vs.* the two-step process or simple redox without coordination, orbital symmetry matching problems *etc.*, whose solution would be important for tailoring of specific catalysts.

1,4-Benzoquinones are useful substrates for the investigation of one-electron redox processes as their radical-anions are quite stable in aprotic media and may be well characterized by EPR and electronic spectroscopy. At the same time, 1,4-benzoquinones are potentially able to coordinate to central metal atoms through the oxygen lone-pair accepting the unpaired electron into the lowest π^* molecular orbital.

However, all reactions between 1,4-benzoquinones with transition metal complexes so far studied produced either dinuclear complexes [L$_n$M-OC$_6$R$_4$-O-ML$_n$] of hydroquinone dianion $^-$O-C$_6$R$_4$-O$^-$, (see *e.g.* refs. 1–4) or π-complexes which have recently been shown to contain the η^4 or η^2-bonded 1,4-quinone ligand [5–8]. No transition metal–1,4-semiquinone radical species has been studied up to the present, in spite of the existence of detailed studies of analogous complexes of non-transition metals [9–11].

In order to study the one-electron oxidative addition producing 1,4-benzosemiquinone complex and the distribution of the unpaired electron in the expected product we have investigated the reaction of 2,6-di-t-butyl-1,4-benzoquinone, DTBQ (I), with a typical metal-centered radical, Co^{II}(CN)$_5^{3-}$. The two tert.-butyl groups are sufficiently bulky to allow



I

the coordination through the C$_4$-oxygen atom only [11]. DTBQ may be therefore supposed to be an excellent substrate for following one-electron redox additions of complexes of those metals forming sufficiently strong bonds with oxygen. As the coordination through C$_1$-oxygen atom is strongly sterically hindered, there is no possibility for formation of dinuclear diamagnetic complexes analogous to those produced by the reactions of other 1,4-benzoquinones with Co(CN)$_5^{3-}$ [1, 2].

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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 [12]. 2,6-di-tert.-butyl-1,4-benzoquinone (DTBQ) was used as obtained from Aldrich Chemical Company, Inc. Bu_4NPF_6 (Ozark-Mahoning Co.) was used as a ground electrolyte in all polarographic measurements. N,N′-dimethylformamide, DMF (Merck) was purified by distillation with benzene under argon atmosphere. Freshly distilled solvent was used in all experiments.

Instrumental

EPR measurements were performed with a Varian E4 X-band spectrometer. Electronic spectra were obtained with a Unicam SP 800 B spectrophotometer. Polarographic measurements were performed either on dropping mercury electrode (DME) or on rotating platinum disc electrode (RPE) using an LP-7e polarograph with the potentiostat modified according to the LP-9 polarograph.

A three-electrode evacuable vessel with Pt-wire auxiliary electrode and Ag/AgCl (10^{-1} mol l^{-1} LiCl) reference electrode was used ($E_{1/2}$ of the Cr(biphenyl)$_2$I reduction with respect to this reference electrode: −0.63 V). Reversibility was tested by means of a Kalousek commutator instrument providing a mercury drop time synchronous with the commutation frequency.

Experimental Technique

Air-sensitive solutions of $Co(CN)_5^{3-}$ in DMF were prepared by dissolution of the appropriate amount of Bu_4NCN in deaerated DMF solution of $CoCl_2$. The resulting very light-yellow solutions were handled under pure argon atmosphere using the Schlenk technique. To stabilize the reaction product, the reaction between $Co(CN)_5^{3-}$ and DTBQ was performed in solutions cooled by solid CO_2/EtOH mixture to approximately −60 °C.

All solutions for spectral or EPR measurements were transferred into the cells in closed vessels under Ar atmosphere and the cells were then sealed off. For polarographic measurements, solutions of $Co(CN)_5^{3-}$ were either added to the vessel under argon atmosphere from a closed burette, where they were previously prepared, or they were generated directly in the polarographic vessel.

Results

$[Bu_4N]_3[Co(CN)_5]$ in DMF Solution

The starting complex was prepared in the DMF solution simply by mixing of appropriate amounts of $CoCl_2$ and Bu_4NCN in DMF under strictly anaerobic conditions. Behaviour of Co^{II}–CN^- system in aprotic solvents, namely acetonitrile, was already described [13] and an equilibrium between tricyano- and pentacyano-complex was proposed. On the other hand, synthesis of solid $[R_4N]_3[Co(CN)_5]$ and $[R_4N]_3[Co(CN)_5O_2]$ were performed in DMF or in hexamethylphosphoramide starting with a Co/CN ratio 1/5 [13].

We have compared spectroscopic as well as electrochemical properties of $Co(CN)_5^{3-}$ in DMF with those observed in CH_3CN [13]. They were found to be analogous. The equilibrium between pentacyano-complex and forms with lower number of CN^- ligands probably establishes more rapidly in DMF than in CH_3CN, as the polarographic kinetic pre-wave ($E_{1/2}$ = −1.98 V) is higher in DMF than that in CH_3CN [*cf.* 13]. However, this kinetic wave almost completely disappears at low temperatures (−15 °C) and in excess of CN^- ions. Reduction of $Co(CN)_5^{3-}$ in DMF occurs at −2.48 V in accordance with the behaviour in CH_3CN [13].

To be sure that the reacting species is actually the $Co^{II}(CN)_5^{3-}$ complex, the Co/CN ratio used was always greater than 5, usually in the range 6–8. The $Co(CN)_5^{3-}$ species is under these conditions well characterized by a sharp, intense absorption spectral band at 285 nm, ϵ = 4500, and broad shoulder in the region 325–350 nm. The absorption spectrum is identical with that obtained in CH_3CN and attributed to $Co(CN)_5^{3-}$ [13]. No absorption bands attributable to other cobalt–cyanide complexes were found under these conditions.

Reaction of $Co(CN)_5^{3-}$ with DTBQ

Mixing the DMF solution of $Co(CN)_5^{3-}$ with substoichiometric amounts of DTBQ solution immediately produces an orange colour which within few minutes turns yellow. Low temperatures strongly stabilize the orange intermediate. At −15 °C the orange colour persists over several hours, at −60 °C it is almost completely stable. The studied reaction occurs immediately even at these low temperatures. The use of low temperatures also hinders any dissociation of CN^- ligands from $Co(CN)_5^{3-}$ complex.

However, it was found that DTBQ itself slowly reacts with free CN^- ions producing $DTBQ^{\bar{\cdot}}$ radical as we proved spectroscopically. This reaction was found to be slow, to such an extent that it cannot compete with the very fast reaction between $Co(CN)_5^{3-}$ and DTBQ, especially in the case when substoichiometric amount of DTBQ is used. This conclusion was confirmed polarographically.

When $Co(CN)_5^{3-}$ reacts with an excess of DTBQ no orange intermediate is observed at laboratory temperature, *i.e.* it may be concluded that DTBQ itself reacts with the primary reaction product.

The studied reaction also proceeds in CH_3CN, but the intermediate (as well as free $DTBQ^{\bar{\cdot}}$) are much less stable than in DMF. In MeOH only a transient, immediately disappearing brown colour appears.

The nature of the primary and final products of the reaction between $Co(CN)_5^{3-}$ and DTBQ was studied by various methods.

EPR Measurements

$Co(CN)_5^{3-}$ complex exhibits a broad unresolved EPR signal in DMF: g = 2.1357, ΔH_{PP} = 10.8 mT. DTBQ itself is not EPR-active.

DMF solutions of $Co(CN)_5^{3-}$ and DTBQ (substoichiometric amount) were mixed inside the EPR cell at low temperature (–60 °C). The cell was then placed into the EPR spectrometer cavity at a temperature of approximately 0 °C. The resulting spectrum (Fig. 1) consists of eight triplets, *i.e.* the splitting arising from the ^{59}Co (I = 7/2) nucleus and from two hydrogen atoms bound at the C_3 and C_5 positions is apparent. EPR parameters are collected in Table I. This spectrum proves that the reaction product is cobalt-bound $DTBQ^{\cdot}$ radical. During a few minutes, the described EPR spectrum decreases and a new signal increases (Fig. 2). This change of EPR spectrum is accompanied by a colour change from orange to yellow. This reaction occurs more readily at laboratory temperature. The original spectrum then disappears within an hour; the new spectrum is completely stable. This new spectrum is formed by one triplet (Fig. 2, Table I) with intensities 1:2:1, *i.e.* only splitting from two hydrogen atoms at the positions C_3, C_5 is observed. This final spectrum is completely identical with that of pure $DTBQ^{\cdot}$ radical (Fig. 3) prepared by the reduction of DTBQ with sodium amalgam in DMF.

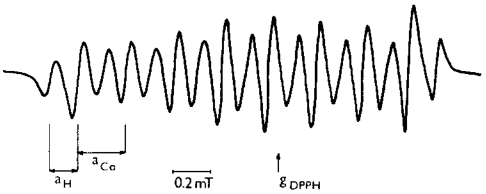


Fig. 1. EPR spectrum of $[Co(CN)_5(DTBQ)]^{3-}$. 2 × 10^{-3} mol l^{-1} $CoCl_2$, 1.5 × 10^{-2} mol l^{-1} Bu_4NCN; immediately before measurement added 4.8 × 10^{-4} mol l^{-1} DTBQ. Temperature approx. 0 °C.

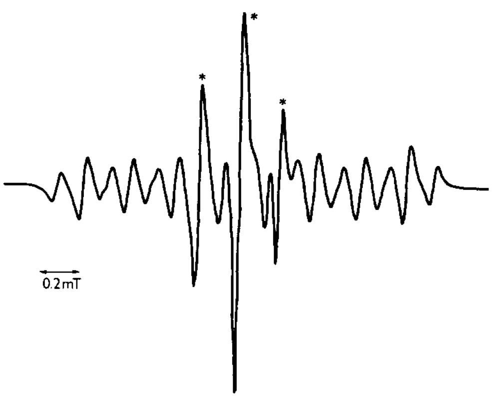


Fig. 2. EPR spectrum of partially decomposed $[Co(CN)_5(DTBQ)]^{3-}$. Conditions as in Fig. 1. Temperature 22 °C. Signals due to free $DTBQ^{\cdot}$ are denoted *.

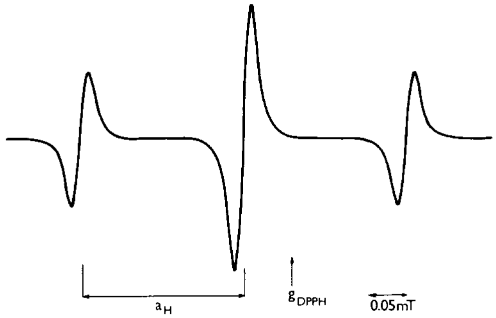


Fig. 3. EPR spectrum of $DTBQ^{\cdot}$ radical in DMF. 1.6 × 10^{-4} mol l^{-1} DTBQ partially reduced by Na-amalgam.

TABLE I. EPR Parameters of DTBQ Radical Adducts and Related Compounds.

Compound	g factor	a_H (mT)	a_{Co} (mT)	Solvent	Ref.
$[Co(CN)_5(DTBQ)]^{3-}$	2.0050	0.140	0.244	DMF	This work
$DTBQ^{\cdot}$	2.0052	0.214	–	DMF	This work
$[Co(CN)_5]^{3-}$	2.1357	–	–	DMF	This work
$[Co(CN)_5O_2]^{3-}$	2.0200	–	1.050	Acetone	13
$[Co(CN)_5(Me_2ClCNO^{\cdot})]^{3-}$	2.0052	–	1.060	MeOH	21
$[Co(CO)_2P(OEt_3)(o\text{-}C_6H_4O_2)]$	2.0030	–	0.610	toluene	14
$DTBQ\cdot SiMe_3$	2.0046	0.112	–	benzene	10
$DTBQ\cdot GeEt_3$	2.0045	0.076	–	benzene	10
$DTBQ\cdot SnMe_3$	2.0044	0.058	–	benzene	10
$DTBQ\cdot PbMe_3$	2.0035	<0.030	–	benzene	10
$DTBQ\cdot PPh_2$	2.0047	0.118	–	benzene	10
$DTBQ\cdot SPh$	2.0047	0.103	–	benzene	10

From the EPR spectra, it may be concluded that the reaction product is a spin-doublet compound containing a Co–DTBQ bond (abbreviated [Co–DTBQ]) which subsequently dissociates producing free DTBQ$^{\cdot-}$ radical, which is stable even in the excess of Co(CN)$_5^{3-}$ (DTBQ was added in substoichiometric amount).

Electronic Spectra

The solutions of Co(CN)$_5^{3-}$ DTBQ were mixed at approximately –20 °C inside a Schlenk-like vessel with a joined quartz spectral cell. The resulting orange solution was then transferred into the cell which was sealed off. At first the UV–VIS spectrum was recorded at 0 °C, further records were carried out at laboratory temperature. Resulting spectra are shown in Figs. 4, 5 and Table II. It may be seen that the overall character of the initial and final spectrum is very similar. The final spectrum is stable over several hours and is identical with that of pure DTBQ$^{\cdot-}$ radical. UV–VIS spectroscopy thus confirms the results obtained by EPR, namely that the reaction product decomposes producing free DTBQ$^{\cdot-}$ radical. There are five isosbestic points present in the spectral record of the reaction. Their existence proves that this reaction occurs as a simple decomposition of the [Co–DTBQ] product with no side-reactions involving strongly light-absorbing species.

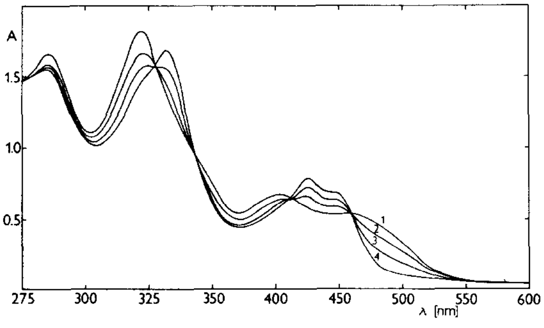


Fig. 4. Electronic absorption spectrum of [Co(CN)$_5$(DTBQ)]$^{3-}$ and its decomposition. 4 × 10^{-4} mol l^{-1} CoCl$_2$, 2.4 × 10^{-3} mol l^{-1} Bu$_4$NCN, 7.4 × 10^{-5} mol l^{-1} DTBQ added at –20 °C. Curve 1: 0 °C, 1.25 min after mixing. Curves 2–4, temperature 28 °C, time after mixing: 2: 7.25 min, 3: 13 min, 4: 40, 50 min.

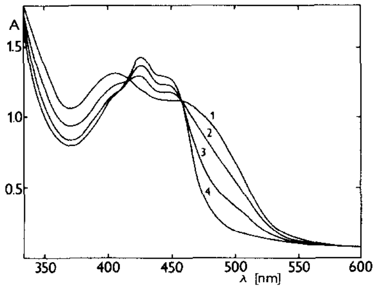


Fig. 5. Electronic absorption spectrum of [Co(CN)$_5$(DTBQ)]$^{3-}$ and its decomposition. Conditions as in Fig. 4. 1.6 × 10^{-4} mol l^{-1} DTBQ added. Recording of curves: 1: 1.62 min, 2: 6 min, 3: 12 min, 4: 40, 50 min.

TABLE II. Electronic Spectral Parameters. λ in nm, ε values are to be multiplied by 10^3. For [Co(CN)$_5$O$_2$]$^{3-}$ spectrum see ref. 13: broad bands, very intense absorption at 325 nm.

[Co(CN)$_5$(DTBQ)]$^{3-}$	DTBQ$^{\cdot-}$	[Co(CN)$_5$O$_2$]$^{3-}$
500 sh	–	–
450 sh, ε = 6.6	446 sh	–
406, ε = 8.4	426, ε = 9.8	–
–	408 sh	403
321, ε = 23.5	331, ε = 22	325

Electrochemistry

Free DTBQ is reduced both at DME and RPE in one-electron waves, at –0.625 V and –1.525 V. The first wave is electrochemically and chemically fully reversible. The second one is, on the other hand, not fully electrochemically reversible and its limiting current is slightly lower than that of the first wave (slope of the log($\bar{i}$/($\bar{i}_L$ – $\bar{i}$)) *vs.* E plot = 79.8 mV; $\bar{i}_L^2/\bar{i}_L^1$ = 0.94). Solutions of DTBQ partially reduced by Na-amalgam, characterized by EPR and UV spectra (Fig. 3–5) as containing DTBQ$^{\cdot-}$, exhibit a one-electron anodic–cathodic reversible wave at –0.625 V and unaffected reduction wave at –1.525 V proving that the product of the first reduction of DTBQ is the free radical DTBQ$^{\cdot-}$. Addition of Bu$_4$NCN to the DTBQ solution causes the formation of the anodic–cathodic wave at –0.60 V (RPE), accompanied with a slow decrease of the overall limiting current with time. Addition of Bu$_4$NCN to partially reduced solution containing DTBQ$^{\cdot-}$ shifts the anodic–cathodic wave at RPE towards positive potentials (E$_{1/2}$ in the range from –0.45 V to –0.50 V depending upon CN$^-$ concentration). The slope of this wave becomes lower and the limiting current decreases with time. Effects of CN$^-$ upon the electrode behaviour of DTBQ were not investigated in more detail.

Bu$_4$NCN is polarographically inactive in the range from +0.7 V to –1.0 V at RPE and from –1.0 V to –2.9 V at DME.

Co(CN)$_5^{3-}$ itself is polarographically oxidized at RPE in a one-electron, irreversible wave at –0.17 V. The corresponding limiting current is diffusion controlled. This wave disappears after aerial oxidation of the solution proving that it is really connected with the Co(II) complex. On DME, Co(CN)$_5^{3-}$ is polarographically inactive in the range from –1 V to –1.90 V (*vide supra*).

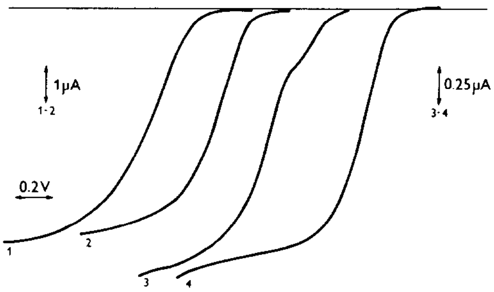


Fig. 6. Anodic polarography of Co(CN)$_5^{3-}$–DTBQ system on RPE. 1: 10^{-3} mol l^{-1} $CoCl_2$, 6.7 × 10^{-3} mol l^{-1} Bu_4NCN, 10^{-1} mol l^{-1} Bu_4NPF_6; T = –63 °C, 2: 9.7 × 10^{-4} mol l^{-1} DTBQ added, 3: immediately after temperature rised to +22 °C, 4: after completion of the reaction. All curves: 1782 rpm, start +0.5 V, curve 1 starts at +0.6 V.

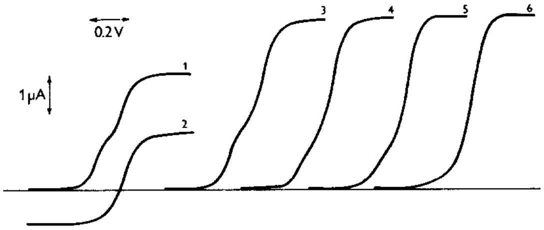


Fig. 7. Cathodic polarography of Co(CN)$_5^{3-}$–DTBQ system on DME. 1: 2 × 10^{-3} mol l^{-1} $CoCl_2$, 1.43 × 10^{-2} mol l^{-1} Bu_4NCN, 10^{-1} mol l^{-1} Bu_4NPF_6, 10^{-3} mol l^{-1} DTBQ, T = –12 °C, drop time 1.44 s, start –1.0 V. 2: commutated wave 1, generation pot. –1.71 V, f = 6.25 Hz, 9 pulses layed on each drop, 3: immediately after temperature rised to 22 °C, 4–6: decomposition of the [Co(CN)$_5$DTBQ]$^{3-}$

Electrochemical behaviour of [Co–DTBQ] species formed by the reaction between Co(CN)$_5^{3-}$ and DTBQ was studied both at RPE and at DME. The anodic behaviour was followed at RPE in solutions prepared by mixing of Co(CN)$_5^{3-}$ with nearly stoichiometric amount of DTBQ (Co/DTBQ = 1.03) at low temperature (–64 °C). After addition of DTBQ to the solution of Co(CN)$_5^{3-}$ the wave at –0.17 V disappears and a new one-electron irreversible wave at –0.20 V is formed (Fig. 6). No anodic wave around –0.6 V appeared, proving that the reaction of DTBQ with uncomplexed CN$^-$ ions does not, under these conditions, compete with the studied reaction. After elevating the temperature up to +22 °C, the wave at –0.20 V decreases and a new anodic wave at –0.46 V appears (Fig. 6). This new wave is identical with that of DTBQ$^{\bullet}$ in the presence of CN$^-$ ions.

The cathodic behaviour of the [Co–DTBQ] was studied at DME in the solutions prepared by mixing of Co(CN)$_5^{3-}$ with DTBQ (DTBQ/Co = ½) in DMF at –12 °C. Upon addition of DTBQ to the solution of Co(CN)$_5^{3-}$, one-electron electrochemically irreversible waves appear at –1.35 V and –1.50 V. Upon commutating this double-wave using a Kalousek commutator with the generation potential –1.71 V, a single commutated wave arises at –1.50 V with the ratio of commutated to diffusion current $\bar{i}_c/\bar{i}_d$ = 1.64 (i_d is the limiting current corresponding to the one-electron wave). This may be explained (assuming that the first reduction at –1.35 V produces free DTBQ$^{\bullet-}$) either by an irreversible electrode reaction, or via fast follow-up decomposition of the primary electrode product, reduced [Co–DTBQ] species. Free DTBQ$^{\bullet-}$ is then reduced in the second wave at –1.50 to DTBQ^{2-}, whose reoxidation is observed in the commutated wave.

After elevating the temperature up to +22 °C, the wave at –1.35 V decreases and the wave at –1.50 V increases with time till a one two-electron wave at –1.52 V is present, corresponding to accidentally coincident two one-electron reductions of the decomposition products: free DTBQ$^{\bullet-}$ radical and a Co^{III}-complex formed by substitution of DTBQ$^{\bullet}$ ligand by another component of the solution.

Polarographic results thus support the conclusions drawn from the spectroscopic studies.

Discussion

The investigated reaction between Co(CN)$_5^{3-}$ and DTBQ in DMF proceeds according to eqn. (1)

$$Co(CN)_5^{3-} + DTBQ \rightarrow [Co(CN)_5DTBQ]^{3-} \qquad (1)$$

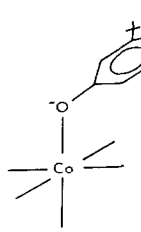
The excess of CN$^-$ ions, together with low-temperature used in all experiments, ensures that the member of Co^{II}–CN$^-$ equilibrium actually reacting with DTBQ in the Co(CN)$_5^{3-}$ complex. The product of the reaction studied may thus be formulated as [Co(CN)$_5$-DTBQ]$^{3-}$.

This complex undergoes a decomposition, in principle a substitution reaction with another component of the solution (traces of H_2O, Cl$^-$ ions, uncomplexed CN$^-$ ions or DMF), releasing free DTBQ$^{\bullet}$ and producing a stable Co^{III} complex. The [Co(CN)$_5$DTBQ]$^{3-}$ species is thus substitutionally labile but it is intrinsincally redox-stable.

There are two points of interest which deserve further discussion: the nature of Co–DTBQ bond, and the detailed mechanism of the interaction between Co(CN)$_5^{3-}$ and DTBQ.

The character of the Co–DTBQ bond may be qualitatively discussed on the basis of the experimental data outlined above. From Table I it may be seen that the EPR parameters, g-factor and a_H, of [Co(CN)$_5$DTBQ]$^{3-}$ are very similar to those of DTBQ–MR$_n$ radical adducts (M = non-transition element).

The g-factor greatly decreases when going from Co(CN)$_5^{3-}$ (unpaired electron localized mainly on the cobalt atom) to [Co(CN)$_5$DTBQ]$^{3-}$ complex, reaching a value almost equal to that of free DTBQ$^{\cdot-}$ radical. The whole EPR spectrum of [Co(CN)$_5$-DTBQ]$^{3-}$ may be looked at as a spectrum of DTBQ$^{\cdot-}$ perturbed by the interaction with the cobalt central atom (Fig. 1–3). This fact leads to the conclusion that the unpaired electron is completely transferred from the Co(CN)$_5^{3-}$ species to DTBQ, forming a Co^{III} complex with ligated DTBQ$^{\cdot-}$ radical. The direct Co^{III}–DTBQ$^{\cdot-}$ bond is unambiguously proved by the observed splitting of the DTBQ$^{\cdot-}$ EPR signal due to the electron spin interaction with ^{59}Co (I = 7/2) nuclear spin. The observed a_{Co} value is very small even in comparison with those of similar Co–radical adducts (see Table I). The unpaired electron has therefore to be localized in the π-orbital of DTBQ$^{\cdot-}$ ligand, its delocalization to the donor oxygen atom and central cobalt atom being very small. The second effect of the coordination of DTBQ$^{\cdot-}$ to Co^{III} seen in the EPR spectrum is manifested by the decrease of a_H splitting constants which is comparable with that observed in other radical adducts of DTBQ$^{\cdot-}$ (Table I). The EPR data indicate that the bonding in [Co(CN)$_5$DTBQ]$^{3-}$ is very similar to that of other DTBQ–MR$_n$ adducts [10, 11]. The DTBQ$^{\cdot-}$ radical can be therefore assumed to be bonded to the Co^{III} central atom via approximately sp^3-lone pair localized on the C$_4$-bonded oxygen atom (II). The unpaired electron is delocalized over the six-membered carbon ring and C$_1$-bonded oxygen atom. Its delocalization over the carbon ring is lower than that in free DTBQ$^{\cdot-}$, *i.e.* the electron spin density on C$_1$-oxygen is higher than that in free DTBQ$^{\cdot-}$.



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The electronic absorption spectrum of the [Co(CN)$_5$DTBQ]$^{3-}$ complex is also essentially a perturbed spectrum of DTBQ$^{\cdot-}$ radical. Maxima of both absorption bands in the complex, corresponding to $\pi \rightarrow \pi^*$ transitions [16, 17], differ only very slightly from those of the free DTBQ$^{\cdot-}$ radical. No d–d transitions were observed. The corresponding low-intensity bands may, however, be expected to overlap with the first broad band of ligated DTBQ$^{\cdot-}$ as follows from the comparison with other Co^{III}(CN)$_5$X complexes [18, 19], the position of d–d bands of which falls within the range covered by this band. No CT band was observed.

The electrochemical oxidation of the ligated DTBQ$^{\cdot-}$ is observed at–0.20 V, *i.e.* by 0.425 V more positive than that of free ligand. However, contrary to the behaviour of free DTBQ$^{\cdot-}$, the ligated radical is oxidized in an electrochemically irreversible (*i.e.* slow) process. This irreversibility is most probably due to a steric hindrance of the electrode–depolarizer interaction caused by the bulky Bu^t groups which cannot operate in the electrode reaction of free ligand. Polarographic data confirm all conclusions drawn from the spectral data: the reaction between Co(CN)$_5^{3-}$ and DTBQ causes the disappearance of the oxidation of Co^{II} and, at the same time, reduction of Co^{III} appears, *i.e.* the characteristic redox behaviour of Co^{II} changes into that of the Co^{III} complex. The same is true concerning DTBQ: the redox behaviour which could be predicted [22] for oxygen coordinated DTBQ$^{\cdot-}$ appears upon the reaction with Co(CN)$_5^{3-}$. The observed electrochemical behaviour is quite different from that of complexes containing π-bonded quinone ligand [6] which cannot exhibit the ligand based oxidation. For π-bonded quinone ligands two reduction steps are observed, the first one being greatly shifted to negative potentials with respect to the free quinone [6].

The polarographic data thus confirm the conclusions concerning the charge distribution in [Co(CN)$_5$-DTBQ]$^{3-}$ species and exclude the possibility of π-bonded DTBQ ligand.

It may be therefore concluded that *[Co(CN)$_5$-DTBQ]$^{3-}$ is a complex of DTBQ$^{\cdot-}$ σ-bonded to Co^{III} central atom through the C$_4$-oxygen atom, the interaction between DTBQ$^{\cdot-}$ π-orbitals and cobalt d-orbitals being rather small.*

The reaction between Co(CN)$_5^{3-}$ and DTBQ involves thus a net electron transfer from the d$_{z^2}$-based molecular orbital of the a$_1$ symmetry of Co(CN)$_5^{3-}$ to π^* orbital of DTBQ. This electron transfer is obviously concerted with coordination of DTBQ to Co-atom, *i.e.* it is a one-electron oxidative addition of DTBQ to Co(CN)$_5^{3-}$. In the course of this process the electron is transferred from the a$_1$ metal orbital (which is of σ-character with respect to the Co^{III}–DTBQ$^{\cdot-}$ bond being formed) to the π-system of the ligand (in most cases of oxidative addition both donor and acceptor orbitals are of σ-character with respect to the bond being formed, as *e.g.* in the case of additions of RX, ArX *etc.* to Vaska complexes).

In the investigated process the electron to be transferred is primarily localized in the a$_1$ orbital, which is the only cobalt localized orbital capable to form a σ-bond with electron lone pairs of the quinone oxygen atom. However, such interaction between the singly occupied a$_1$ orbital with approximately sp^2-hybridized, doubly occupied lone pair orbital of quinone oxygen atom would result in the formation of σ-bond and a singly occupied σ-antibonding orbital, *i.e.* in a process requiring high activation energy and leading to very unstable product.

The observed reaction is very fast [20], *i.e.* it has to be a completely allowed process. However, no interaction involving oxygen lone-pair would produce low-energy transition state. The only possible low-energy interaction is that between singly occupied a_1 orbital and π^* orbital (LUMO) of the quinone. This interaction can be mediated by the overlap between the a_1-orbital and oxygen p-orbital involved in quinone π-system. The plane of the quinone molecule has to be parallel with the basal plane of the Co(CN)$_5^{3-}$ square pyramid to make the described orbital interaction effective. During mutual approach of the reactants, the a_1–π interaction strengthens and net electron density is transferred from the cobalt atom to the quinone. This electron transfer induces a complete redistribution of the ligand π-system. The six membered carbon ring of the quinone molecule reaches a nearly aromatic character, the C_4=O double bond is disrupted, the p orbital of the interacting oxygen is shut out from the π-system and turns into approximately sp^3, doubly occupied orbital forming σ-bond with the cobalt atom. The odd electron is localized mainly on the C_1-oxygen atom and is only partially delocalized over the carbon ring and C_1–O bond. This is in accordance with observed decrease of a_H values when going from free to coordinated DTBQ$^{\cdot-}$.

The outlined picture of the Co(CN)$_5^{3-}$–DTBQ primary interaction may be valid also for oxidative additions of O_2 or NO, producing bent M–NO species and also, in the case of one-electron oxidative addition, of aliphatic nitroso compounds to Co(CN)$_5^{3-}$ [21]. It may be regarded as a general pathway operating in oxidative additions involving the electron transfer from σ metal orbitals to ligand π orbitals.

It is also noteworthy that no reaction proceeds between Co(CN)$_5^{3-}$ and free DTBQ$^{\cdot-}$. The existence of dinuclear [(CN)$_5$Co(OC$_6$H$_4$O)Co(CN)$_5$]$^{6-}$ species and of [Co(CN)$_5$OC$_6$H$_4$OH]$^{3-}$ [1, 2] shows that a cobalt–hydroquinone bond can, in principle, exist. The unreactivity of DTBQ$^{\cdot-}$ toward Co(CN)$_5^{3-}$ may be therefore explained by the delocalization of the DTBQ$^{\cdot-}$ unpaired electron over the carbon ring. The DTBQ$^{\cdot-}$ radical is thus not able to add another electron via the σ–π mechanism described above and its Lewis basicity is too low for simple coordination on relatively weakly acidic Co(CN)$_5^{3-}$.

Formation of a dinuclear complex analogous to that of unsubstituted *p*-quinone [1, 2] is, in the studied case, impeded by the steric hindrance of the C_1-oxygen atom, *i.e.* [Co(CN)$_5$DTBQ]$^{3-}$ radical species is kinetically stabilized. The reaction of Co(CN)$_5^{3-}$ with unsubstituted *p*-OC$_6$H$_4$O producing dinuclear [(CN)$_5$Co(OC$_6$H$_4$O)Co(CN)$_5$]$^{6-}$ is assumed to proceed via [Co(CN)$_5$(OC$_6$H$_4$O)]$^{3-}$ unstable intermediate [1, 2, 20]. The odd electron in this species could be supposed, by analogy with [Co(CN)$_5$DTBQ]$^{3-}$, to be localized predominantly on the uncoordinated oxygen atom. The reaction of [Co(CN)$_5$(OC$_6$H$_4$O)]$^{3-}$ intermediate with the second molecule of Co(CN)$_5^{3-}$ is therefore a common oxidative addition producing a cobalt–oxygen σ-bond. In the reaction of Co(CN)$_5^{3-}$ with unsubstituted *p*-benzoquinone, the quinone is thus reduced stepwise by two one-electron oxidative additions involving both oxygen atoms, and producing hydroquinone ligand bound to two cobalt atoms in the [(CN)$_5$Co(OC$_6$H$_4$O)Co(CN)$_5$]$^{6-}$ dinuclear complex. An interesting question thus arises, whether it is possible to reduce *p*-quinones by two electrons directly via only one oxygen atom. This and related problems are under investigation.

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