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Redox Potentials and Charge Transfer Spectra of Catecholate and Semiquinone Adducts of a Cobalt–Tetraazamacrocyclic Complex

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Abstract

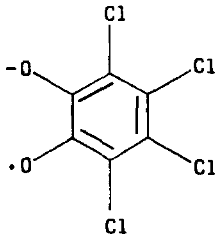
Catecholate and semiquinone complexes of cobalt(II) and cobalt(III) with the macrocyclic ligand DL-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane have been synthesized and characterized. The dioxolene ligands are 3,5-di-t-butylcatechol and tetrachlorocatechol. Evidence is presented that oxidation of cobalt(II) to cobalt(III) occurs before oxidation of catecholate to semiquinone and quinone. The energies of the charge transfer bands either LMCT and MLCT are discussed in terms of electrochemical potentials.

Introduction

At present there is a large interest in the possibilities offered by molecules which can exist in different states as possible active sites for molecular electronic devices [1, 2]. So, for instance, systems exhibiting spin–crossover behavior [3–5] or mixed valence character [6–9] are currently actively investigated.

Metal–dioxolene complexes provide an alternative route to have two or more states differing so little in energy that they become accessible through small thermal or electromagnetic perturbations [10, 11]. These systems appear to be particularly worthy of investigation because (i) the ligand can bind in three different oxidation states, namely quinone, semiquinone or catechol, and (ii) several different metal oxidation states can be stabilized.

In order to determine the conditions under which the different oxidation states of metals and ligands are stabilized, we have used metal macrocyclic complexes which can bind to one dioxolene molecule at a time and can give different coordination environments [12–14]. We wish to report here the synthesis and the spectral and magnetic properties of. solid compounds containing complexes of general formula $Co(CTH)(diox)^{n+}$ complexes ($n = 0$, 1, 2; CTH = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) where diox is an anionic *o*-dioxolene ligand either catecholate or semiquinonate deriving from 3,4,5,6-tetrachlorocatechol (TCCat and TCSQ (I)) and 3,5-di-t-butylcatechol (DTBCat and DTBSQ (II)). Hence it will be shown how the coupling of electrochemical measurements and electronic spectra can provide fundamental insight into the redox equilibria of metal dioxolene complexes.



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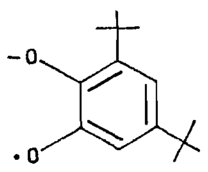

II

Experimental

Materials

3,4,5,6-Tetrachlorocatechol ($TCCatH_2$), 3,4,5,6-tetrachlorobenzoquinone (TCQ), 3,5-di-t-butylcatechol ($DTBCatH_2$) and 3,5-di-t-butyl-*o*-benzoquinone (DTBQ) were used as received. The tetraazamacrocycle CTH was prepared according to the literature method [15].

$Co(CTH)Cl_2$

Three mmol of $Co(H_2O)_6Cl_2$ were refluxed for 0.5 h in 30 ml of a dimethylformamide–triethylorthoformate 2/1 mixture. The resulting solution was deaerated and added to a warm dimethylformamide solution containing 4 mmol of CTH. The color changed from blue to violet. Blue violet crystals appeared upon concentration. The product was filtered under nitrogen, washed with ethanol/diethyl ether mixtures and then dried under nitrogen.

Synthesis of the Dioxolene Adducts

Co(CTH)(TCCat)

$Co(CTH)Cl_2$ (1 mmol) was suspended in deaerated methanol (20 ml) and 1 mmol of $TCCatH_2$ was then

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added as solid. The addition of 2 mmol of NaOH in methanol induced the precipitation of yellow crystals, which were collected, washed with methanol and dried under nitrogen (yield 79%). The compound is air stable when dry. *Anal.* Found: C, 44.12; H, 6.35; N, 9.15. Calc. for $C_{22}H_{36}Cl_4CoN_4O_2$: C, 44.53; H, 6.11; N, 9.44%.

Co(CTH)(TCCat)PF$_6$

A solution of TCQ (1 mmol) in 20 ml of ethanol was added under nitrogen to a suspension of Co(CTH)Cl$_2$ (1 mmol) in the same solvent (20 ml). The resulting solution was warmed for 0.5 h. The addition of an aqueous solution of KPF$_6$ induced the precipitation of a microcrystalline material, which was washed with ethanol (yield: 64%). *Anal.* Found: C, 35.80; H, 5.16; N, 7.29. Calc. for $C_{22}H_{36}Cl_4CoF_6N_4O_2P$: C, 35.78; H, 4.92; N, 7.59%.

Co(CTH)(DTBCat)PF$_6$

A solution of DTBQ (0.5 mmol) was added under nitrogen to a suspension of Co(CTH)Cl$_2$ (1 mmol) in ethanol. The resulting solution was refluxed for 0.5 h. The addition of an aqueous solution of KPF$_6$ induced the precipitation of brown crystals, which were recrystallized from methanol (yield: 40%). *Anal.* Found: C, 50.77; H, 8.29; N, 7.68. Calc. for $C_{30}H_{56}CoF_6N_4O_2P$: C, 50.84; H, 7.96; N, 7.91%.

Co(CTH)(DTBSQ)Cl$_{0.5}$*(PF*$_6$*)*$_{1.5}$*·H*$_2$*O*

This compound was prepared in a similar fashion to the previous one using a stoichiometric ratio Co(CTH)Cl$_2$/DTBQ 1:1. Violet crystals were obtained by recrystallization from methanol (yield: 69%). *Anal.* Found: C, 44.40; H, 7.30; N, 7.05; Cl, 2.11. Calc. for $C_{30}H_{58}Cl_{0.5}CoF_9N_4O_3P_{1.5}$: C, 44.10; H, 7.16; N, 6.86; Cl, 2.17%.

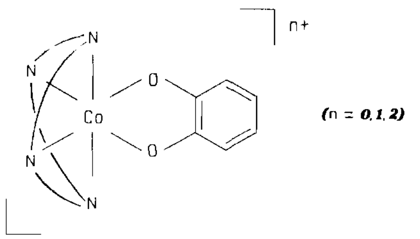
Physical Measurements

Physical measurements were carried out as previously described [12].

Results

The Co–CTH^{2+} complex has been chosen for this investigation because of its expected reactivity towards electrophiles and because of the ability of the ligand to adopt a folded configuration [12, 16]. Indeed the reaction of this complex with the two dioxolene ligands considered in this study yields six-coordinate cobalt derivatives containing a single chelated dioxolene according to the following.

Crystalline compounds of formula Co(CTH)(DTBSQ)Cl$_{1/2}$(PF$_6$)$_{3/2}$ and Co(CTH)(TCCat)PF$_6$ were obtained as products of the oxidative addition of the appropriate quinone to Co(CTH)Cl$_2$ in 1:1 stoichiometric ratio. The different nature of the reaction products, i.e. catecholate or semiquinonate, is due to the different oxidative properties of the two semiquinone adducts. Indeed the Co(CTH)(TCSQ)$^+$ complex, which is formed in the oxidative process, presumably reacts with the solvent giving the catecholate derivative as a further reaction product. This does not occur for the Co(CTH)(DTBSQ)$^+$ cation, but when the oxidative addition is carried out in the presence of an excess of the reducing Co(CTH)Cl$_2$ complex, the complex Co(CTH)(DTBCat)PF$_6$ can be isolated.



The reaction of TCCatH$_2$ in alkaline medium with the Co(CTH)$^{2+}$ complex, yields the orange–yellow crystalline Co(CTH)(TCCat), which is readily oxidized by aerial dioxygen.

The above formulation of the reaction products follows from spectral and magnetic evidence. Co(CTH)(TCCat) has a $\mu_{\mathrm{eff}} = 4.76\ \mu_B$ consistent with a high-spin six-coordinate cobalt(II) ion. Co(CTH)(DTBSQ)Cl$_{1/2}$(PF$_6$)$_{3/2}$ is paramagnetic ($\mu_{\mathrm{eff}} = 1.79\ \mu_B$) and its ESR spectrum (Fig. 1) is consistent with the presence of one unpaired electron mainly localized on the dioxolene ligand interacting with a cobalt(III) ion ($g = 2.00$, $A_{\mathrm{Co}} = 9.5$, $A_{\mathrm{H}} = 2.0$) [17]. Co(CTH)(DTBCat)PF$_6$ and Co(CTH)(TCCat)PF$_6$ are diamagnetic, according to the nature of cobalt(III) derivatives of closed-shell ligands. IR spectroscopy does not provide significant information about the nature of these dioxolene complexes. Indeed the strong ligand absorptions at 1450 cm^{-1} do not allow

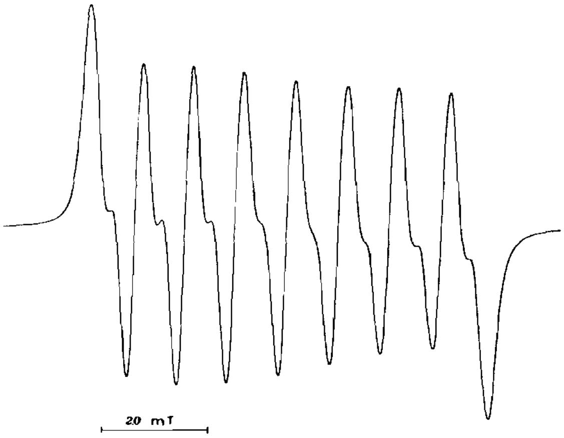


Fig. 1. ESR spectrum of [Co(CTH)(DTBSQ)](PF$_6$)$_2$ in acetonitrile solution (T room).

unambiguous assignment of absorptions characterizing either catecholates or semiquinones [18]. However the intensity of the band at *c.* 1250 cm^{-1}, where absorptions due to the C–O stretching mode are expected to occur, is significantly weaker in the semiquinone derivative than in corresponding catecholate, thus supporting the proposed assignment [14, 19]. Further evidence of the nature of the cobalt–dioxolene adducts arises from the features of the electronic spectra to be discussed below.

Electrochemistry

Cyclic voltammograms of deaerated acetonitrile solutions of $Co(CTH)(DTBCat)PF_6$ show three redox couples (Fig. 2) at –0.69, 0.235 and 1.16 V versus SCE. Coulometric experiments indicate that all the reaction processes are monoelectronic. The first two couples exhibit the typical features of reversible electron transfer processes, the i_c/i_a ratio being equal to 1 and the peak to peak separation approaching the value of 60 mV at low scan rates [20]. The third couple is irreversible.

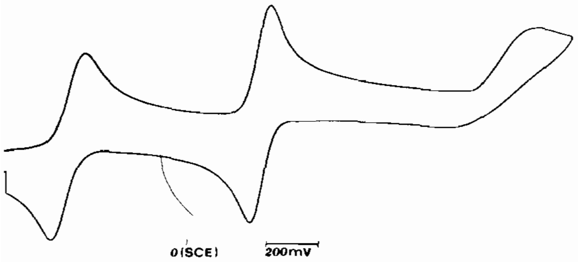


Fig. 2. Cyclic voltammogram of $[Co(CTH)(DTBCat)]PF_6$ in acetonitrile 0.1 M NBu_4PF_6. Scan rate 0.1 V s^{-1}, reference electrode SCE.

On the basis of spectral evidence, the couple occurring at negative potential is associated with the metal centered electron transfer process

$$Co(III)(CTH)(DTBCat)^{+} \xrightleftharpoons{+e^{-}} Co(II)(CTH)(DTBCat)$$

whereas the couples occurring at positive potentials are associated to electron transfer processes involving the dioxolene ligand, i.e.

$$Co(III)(CTH)(DTBSQ)^{2+} \xrightleftharpoons{+e^{-}} Co(III)(CTH)(DTBCat)^{+}$$

and

$$Co(III)(CTH)(DTBQ)^{3+} \xrightleftharpoons{+e^{-}} Co(III)(CTH)(DTBSQ)^{2+}$$

leading to the formation of the semiquinone adduct $Co(CTH)(DTBSQ)^{2+}$ and the unstable quinone $Co(CTH)(DTBQ)^{3+}$. These findings are in agreement with the chemical behavior exhibited by other cobalt–dioxolene derivatives [21, 22].

Similar conclusions can be drawn from the analysis of the voltammograms of $Co(CTH)(TCCat)PF_6$, which show again three redox processes. The first one occurring at negative potentials is non-reversible (E_{red} = –0.74 V, E_{ox} = –0.3 V) and is attributed to the metal centered Co(III)–Co(II) couple. The second occurring at 0.83 V is reversible and is attributed to the ligand centered semiquinone–catecholate couple, whereas the third occurring at 1.78 V may be associated with the irreversible semiquinone to quinone oxidation.

Electronic Spectra

The electronic spectra of acetonitrile solutions containing the $Co(III)(CTH)(diox)^{n+}$ chromophores (n = 1, 2; diox = catecholate, semiquinone) are shown in Figs. 3 and 4. The spectral parameters are shown in

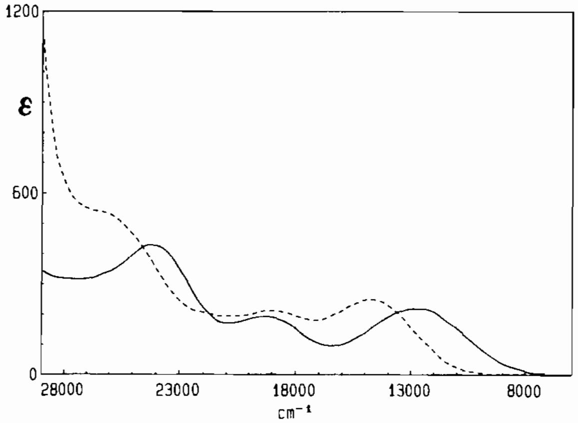


Fig. 3. Electronic spectra of $[Co(CTH)(DTBCat)]PF_6$ (——) and $[Co(CTH)(TCCat)]PF_6$ (– – –) in acetonitrile solution.

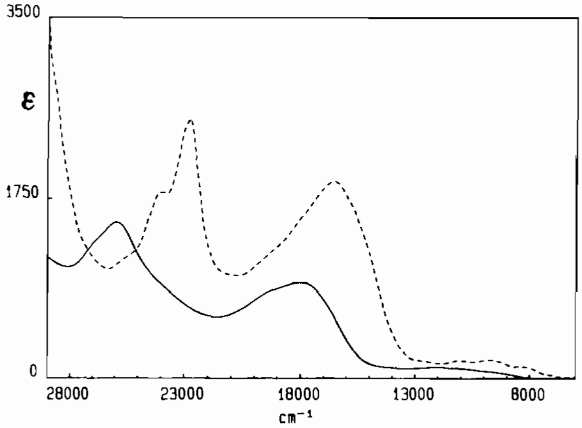


Fig. 4. Electronic spectra of $[Co(CTH)(DTBSQ)]^{2+}$ (——) and $[Co(CTH)(TCSQ)]^{2+}$ (– – –) complexes in acetonitrile solution.

TABLE 1. Electronic spectra of Co(III)(CTH)(diox)$^{n+}$ complexes ($n = 1, 2$) in acetonitrile solution

Compound	Absorption maxima[a]
Co(III)(CTH)(DTBCat)$^+$	12800(2.37); 19300(2.32); 24200(2.66); 26400sh; 32700(4.02); 36700(3.95)
Co(III)(CTH)(TCCat)$^+$	14800(2.39); 18800(2.31); 26200(2.72); 31400(3.93); 32400sh
Co(III)(CTH)(DTBSQ)$^{2+}$	12000(2.23); 18100(2.99); 19400sh; 24000sh; 26000(3.18); 27000sh; 34000sh
Co(III)(CTH)(TCSQ)$^{2+}$	8400sh; 9600(2.26); 10800sh; 16500(3.31); 19400sh; 22700(3.39); 23900(3.24); 25400sh; 31400sh

[a] In cm^{-1}, log ϵ in parentheses; sh = shoulder.

Table 1. Solutions containing the species Co(III)(CTH)(TCSQ)$^+$ were obtained by controlled potential electrolysis of the precursor catecholate derivative.

Owing to their extreme sensitivity towards oxidation, we cannot obtain suitable spectral parameters for the solution containing cobalt(II)–catecholate complexes. Complications arise by the overlap of the expected bands in the visible region with those more intense of contaminating cobalt(III) species. The features of the spectra in the UV region are similar to those observed for the nickel(II)– and zinc(II)–catecholate analogues.

Cobalt(III)–catecholate complexes

The spectra of these complexes show three bands of comparable intensity in the visible region of the spectrum at 12 800, 19 300 and 24 200 cm^{-1}, with a shoulder at 26 400 cm^{-1} for the Co(III)(CTH)(DTBCat)$^+$ chromophore and at 14 800, 18 800 and 26 200 cm^{-1} for Co(III)(CTH)(TCCat)$^+$. *cis*-Octahedral cobalt(III) derivatives are expected to exhibit two allowed transition related to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ occurring in O_h symmetry. On the basis of ligand field considerations and comparison with literature data [23], we attribute the transitions at 19 300 and 18 800 cm^{-1} to the first expected transition from the $^1A_{1g}$ ground state to the in practice unsplit $^1T_{1g}$ excited state. The two bands occurring at higher and lower energies exhibit a blue shift on passing from DTBCat to TCCat and therefore are attributed to ligand-to-metal charge transfer transitions. The second allowed d–d metal transition, i.e. $^1A_{1g} \rightarrow {}^1T_{2g}$, originates probably the shoulder at 26 400 cm^{-1} in the spectrum of the Co(III)(CTH)(DTBCat)$^+$ complex and is obscured in the spectrum of the Co(III)(CTH)(TCCat)$^+$ by the charge transfer transition. If this assignment is correct, the crystal field parameters $10Dq$ and C of the Co(III)(CTH)(DTBCat)$^+$ chromophore can be estimated, the energy separation between the $^1T_{1g}$ and $^1T_{2g}$ states being approximately $4C$ and the energy of the $^1T_{1g}$ state being $10Dq - C$. The values of $Dq = 21\,100$ cm^{-1} and $C = 1775$ cm^{-1} which are found are in full agreement with those observed for other Co(III)N$_4$O$_2$ chromophores [23].

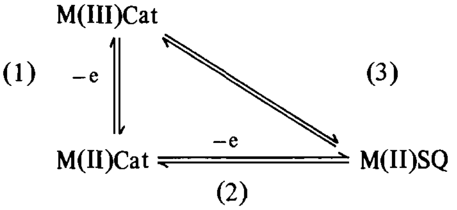
Cobalt(III)–semiquinone complexes

The spectra of these complexes are very rich in bands which may be assigned taking into account the internal transitions of the semiquinone ligands. We have previously shown [14] that, in addition to the transitions occurring in the UV region, which are in practice the same as catecholate ligands, the spectra of the semiquinone complexes are characterized by at least two bands falling in the visible region. They are attributed to the transitions from internal electronic levels to the singly occupied 3b$_1$ level (HOMO in catecholate). Indeed transitions occurring at 12 000 and 9600 cm^{-1} in the spectra of the Co(CTH)(DTBSQ)$^+$ and Co(CTH)(TCSQ)$^+$, respectively, are assigned to the 9a$_1$ → 3b$_1$ transitions (n → π^* in character), and those at 26 000 (DTBSQ) and 23 900 (TCSQ) cm^{-1} to 2a$_2$ → 3b$_1$ transitions ($\pi \rightarrow \pi^*$ in character). Again, as observed in other semiquinone derivatives [14, 24], both transitions exhibit a vibrational progression presumably assigned to the C–O stretching mode.

The two intense bands occurring at 18 100 (DTBSQ) and 16 500 (TCSQ) cm^{-1} cannot be assigned to internal transition of the dioxolene ligand and therefore we assign them as metal to ligand charge transfer (MLCT). The shoulder occurring at 19 400 cm^{-1} in both the spectra may be reasonably assigned, as in the previous cobalt(III)–catecholate derivatives, to the lowest energy metal centered transition.

Discussion

One-electron oxidation of a metal(II)–catecholate adduct may in principle yield either metal(II)–semiquinonate or metal(III)–catecholate as products, depending on the balance of the free energy changes of the two processes. The relative stabilities of the different species are determined by the equilibria shown below:



The equilibrium connecting M(III)Cat and M(II)SQ corresponds to an internal electron transfer.

Actually cobalt is borderline between earlier transition metal ions, for which one-electron oxidation of metal(II) catecholates yields metal(III)–catecholates [24] and later transition metal ions, which yields metal(II)–semiquinonates [12, 14]. Information on equilibrium (1) is experimentally available for cobalt(III), but not on equilibrium (2). However we have found [12, 14] that the redox potential relative to (2) is roughly constant in a series of semiquinones metal complexes, suggesting that the metal ion provides only an electrostatic potential which gives a constant shift to the redox potential of the dioxolene molecules. Similar results were obtained also for tripositive ions [24], where the shifts of the potentials were found to be larger.

If we assume that the potential relative to (2) for cobalt(II) is the same as for nickel(II), which is experimentally available, we see that indeed the potentials for (1) and (2) are rather close to each other for cobalt(II) dioxolene complexes. In fact, following this assumption, we can assign to Co(II)-(CTH)(DTBSQ)/Co(II)(CTH)(DTBCat) and Co(II)-(CTH)(TCSQ)/Co(II)(CTH)(TCCat) couples the values of −0.6 V versus SCE and 0.0 V versus SCE, respectively, as found for the analogues nickel(II) and zinc(II) derivatives [14].

Equilibrium (1) is dominant in the present cobalt complexes, but by using coligands which stabilize less cobalt(III) it is conceivable to make equilibrium (2) the favorite. It is also possible to have systems in which the two equilibria compete in such a way that one dominates at high temperature and the other at low temperature. This indeed has already been found to be the case for the Co(bipy)(DTBCat)(DTBSQ) derivative [25].

The difference between the observed redox potentials for the couples Co(III)(CTH)(cat)$^+$/Co(II)(CTH)-(cat) and the values assumed for the couples Co(II)-(CTH)(sq)$^+$/Co(II)(CTH)(cat) yields the free energy changes associated to the internal electron transfer (3) which is the energy of the charge transfer transition between the ground state and the first charge transfer excited state in their equilibrium vibrational states (i.e. the O–O′ transition) and solvent equilibrium environment [23, 26]. The calculated differences are 0.1 and 0.5 eV for DTBCat and TCCat, thus indicating that LMCT transitions are expected to occur at low energies, as observed in the electronic spectra. The fact that the observed values are significantly higher that the calculated ones can be explained considering that:

(i) the observed CT transitions involve low-spin cobalt(II) as the excited state, whereas the redox equilibria are related to high-spin cobalt(II) species;

(ii) for largely different states, such as the ones involved here, the adiabatic electronic transitions do not correspond to the O–O′ transition, but to highly excited vibronic states of the upper level;

(iii) the difference in solvation energy between the ground and the excited state is expected to be not neglectable.

The HOMO in both catecholate and semiquinone has π^* character [14, 22, 27] and is orthogonal to the empty σ orbitals of the cobalt(III) ion. Therefore transitions involving these orbitals are expected to have a low intensity. On this basis the low energy bands occurring in Co(CTH)(cat)$^+$ chromophores may be reasonably assigned to the $3b_1$(cat) → e_g(Co) transition, while the high energy bands may be assigned to electron transfers from the oxygen lone pair (i.e. the $9a_1$) level of the catecholate and the same empty metal orbitals.

The oxidation of the ligand to semiquinone removes one electron from the $3b_1$ orbital, thus increasing its energy and stabilizing 3d metal orbitals. The intense MLCT observed in the spectra of these cobalt(III)–semiquinone complexes may be reasonably assigned to electron transfer from the metal t_{2g} orbitals to the singly occupied $3b_1$ orbital. As observed for other chromophores [12, 14, 24], this transition is symmetry allowed and the overlap between metal and ligand orbitals is large, thus supporting the strong transition moment of the band.

The spectroscopic data therefore support the results of the electrochemical data indicating that the energy levels of metal and ligand orbitals are very close. In this respect therefore the cobalt dioxolene system should be highly considered for designing compounds characterized by peculiar bistability properties. An extensive research program in this direction is actually in hand in this laboratory.

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