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Electrochemical and electrocatalytic studies of the *N,N'*-(1*R*,2*R*)-(–)-1,2-cyclohexylenebis(salicylideneiminato)cobalt(II) complex

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Abstract The electrochemical properties and catalytic activity of a Co(II) complex with the optically active Schiff base derived from (1*R*,2*R*)-(–)-cyclohexanediamine and salicylaldehyde have been studied in non-aqueous solutions. When dissolved in deoxygenated non-aqueous solutions, the complex exhibits reversible redox properties for the Co(II)/Co(III) couple. Electrochemical reduction of oxygen and oxidation of cobalt(II) was observed on cyclic voltammograms of solutions containing both dioxygen and the Schiff base-cobalt(II) complex. An anodically formed film on a platinum electrode, studied by means of X-ray photoelectron spectroscopy, revealed the presence of the oxidized Co(III) species. Cyclic voltammetry of oxygenated solutions examined after a period of time indicates an electrochemical activity of coordinated superoxo/peroxo species in the 0.7–1.1 V potential range. In the presence of 4-methyl-1-cyclohexene the cyclic voltammetry curves reveal changes similar to those caused by the removal of oxygen. The GC-MS technique was used to identify some of the products formed by the catalytic oxidation of cyclohexene and 4-methyl-1-cyclohexene.

Key words Cyclic voltammetry · Cobalt(II)-Schiff base complex · Oxygen adducts · Electropolymerization · Electrocatalytic oxidation

Introduction

A knowledge of the chemical interactions between dioxygen and transition metal complexes is relevant for

understanding the transport and activation of oxygen in living organisms. Likewise, it is important to verify the mechanism of molecular oxygen activation in electrocatalytic reduction [1, 2] and in catalytic oxidation [3, 4]. Schiff base complexes are interesting catalysts for the oxygenation of hydrocarbons [5]. Such reactions are not yet fully understood even though the reduction of dioxygen in aqueous and non-aqueous solutions has been receiving a great deal of attention owing to its applications in fuel cells and batteries, and its involvement in biological reactions [6].

The electrochemistry of Schiff base metal complexes in aqueous and non-aqueous media has been extensively studied [7, 8, 9, 10]. It has been reported that transition metal planar chelates of the N_4 or N_2O_2 type can form adducts with dioxygen via charge transfer from the central metal ion to oxygen [11, 12, 13, 14]. Formation of 1:1 and 1:2 aggregates of O_2 with Co(salen) and similar complexes has been confirmed [15, 16, 17]. It has been noted that the reduction potential assigned to the coordinated oxygen in the complex is shifted towards the positive potential in relation to the free oxygen molecule, which indicates that the reduction of oxygen is easier [3, 4, 8]. Additionally, electrochemical oxidation of complexes during anodic polarization produces at the electrode surface a film of variable composition that has not yet been completely characterized. Both auto-oxidation and electrochemical oxidative polymerization have been considered to explain this phenomenon [10, 14, 15]. In this paper we will describe further results of X-ray photoelectron spectroscopy (XPS) studies of the film obtained.

Further understanding of dioxygen interaction with cobalt chelates in solution and at the electrode surface requires additional information about the influences of ligand and solvent. We have therefore decided to study the electrochemical behaviour of *N,N'*-(1*R*,2*R*)-(–)-1,2-cyclohexylenebis(salicylideneiminato)cobalt(II), $[Co^{II}(-)\{chxn(sala)_2\}]$, in oxygenated and deoxygenated solvents.

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Experimental

Materials

Ethanol (EtOH), acetonitrile (MeCN) and dichloromethane (CH₂Cl₂), all 99.9% HPLC grade (Sigma-Aldrich), as well as lithium perchlorate (LiClO₄, p.a., Janssen) and tetrabutylammonium tetrafluoroborate (Bu₄NBF₄, p.a., Fluka) were used as received. The cobalt(II) complex was synthesized as reported [20]. 4-Methyl-1-cyclohexene (pure, Janssen) and cyclohexene (99%, Fluka) were used as received.

Instrumental

Voltammetric measurements were performed with an Autolab (Eco Chemie) modular electrochemical system equipped with a PSTAT 10 potentiostat and driven by GPES3 software (Eco Chemie). A three-electrode cell was used and the solution was kept under argon at room temperature. Bubbling argon or oxygen (pre-saturated with solvent) through the solution for 1 h ensured its saturation. The approximate concentration of dissolved O₂ in solutions can be assumed according to the literature data: 6.3 mM in EtOH [21], 8.1 mM in MeCN [6] and 10.1 mM in CH₂Cl₂ [21]. The concentration of oxygen in de-aerated solvents was below detection (no color changes in the complex solution from orange to dark red). Platinum, gold and glassy carbon mini-disc electrodes (1 mm diameter) from Cypress System were used as working electrodes. Platinum wire was employed as the counter electrode, and Ag/AgCl/KCl(sat.) was the reference electrode. All potentials are quoted with respect to this reference.

XPS measurements

The XPS measurements were carried out with an EscaLab 210 (VG Scientific) spectrometer using non-monochromatized Al K α radiation (1486.6 eV), the source being operated at 15 kV and 34 mA. An 8 mm diameter Pt disc was used as the working electrode and subjected to cyclic voltammetry. The cyclic voltammograms become constant when cycled for 10–15 cycles. The Pt disc was removed from the electrolyte solution, washed, and the XPS spectrum recorded. High-resolution scans were performed over the 776–792 eV range (Co 2p_{3/2} spectrum). After subtraction of the base line (Shirley-type), curve fitting was performed using the non-linear least-squares algorithm and assuming a Gaussian/Lorentzian mix of variable peak shape proportion. Peak fitting was repeated until an acceptable error was obtained (5%). The positions of the resolved peaks were determined in accordance with the literature data [22] and empirically derived values.

Catalytic runs

The catalytic reactions were performed in CH₂Cl₂ and EtOH solutions at 20 °C. Alkene (16 mmol) with [Co^{II}(-){chxn(salal)₂}] (8 μ mol) in solvent (25 mL) was bubbled through with air for up to 24 h and the solution was GC analyzed with ITD-800 Finnigan MAT GC-MS equipment, a capillary column (30 m \times 0.249 mm) and a DB-17 liquid phase.

Results and discussion

Electrochemical studies of the Co(III)/Co(II) redox couple

Cyclic voltammograms (CVs) of [Co^{II}(-){chxn(salal)₂}] were recorded with the Pt, Au and glassy carbon electrodes in the 0.00–0.50 V potential range (vs. Ag/AgCl) using scan rates from 0.01 to 0.40 V s⁻¹ in de-aerated EtOH, MeCN and CH₂Cl₂. The [Co^{II}(-){chxn(salal)₂}]/[Co^{III}(-){chxn(salal)₂}]⁺ electrochemical couple between 0.00 and 0.50 V was almost reversible (Fig. 1a, Table 1). Because the best reversibility was found on the Pt electrode, this was the one chosen for further experiments. The anodic (*i*_{p,a}) and cathodic (*i*_{p,c}) peak currents in de-aerated solutions depend linearly on the complex concentration (from 0.2 to 1.3 mM), and also on the square root of the scan rate (from 0.005 to 0.2 V s⁻¹), which may be related to the diffusion-controlled processes. The CV data (Table 1) ($\Delta E_p = \text{abs}[E_{p,c} - E_{p,a}] \approx 60$ mV, $i_{p,a}/i_{p,c} \approx 1$) for experiments performed under argon correspond to the chemically reversible charge-transfer process (*E*_r). These processes are usually assumed to be a single-electron reduction/oxidation Co(III)/Co(II) couple [23, 24].

The CVs of [Co^{II}(-){chxn(salal)₂}] solutions (0.1 M, LiClO₄, EtOH or 0.1 M, Bu₄NBF₄, MeCN) recorded after saturation with oxygen for 1 h revealed peaks ($\Delta E_p > 70$ mV, $i_{p,a}/i_{p,c} > 1$), which indicates the greater irreversibility of the process under investigation (Table 1). The significant decrease in *i*_{p,a} and *i*_{p,c} currents (Fig. 1b) may correspond to the interactions between the complex and oxygen molecules. The CV curve measured after 24 h of saturation with oxygen (Fig. 1c) displays only a broad anodic wave between 0.20 and 0.40 V

Table 1 Selected cyclic voltammetric data for the Co(III)/Co(II) complex couple in different electrochemical systems

Electrochemical system		Measured under argon					Measured during contact with air (1 h)			
Electrolyte/solvent	Electrode	<i>E</i> _{p,a} (V) ^a	<i>E</i> _{p,c} (V) ^a	<i>n</i> ^b	<i>i</i> _{p,a} / <i>i</i> _{p,c}	<i>E</i> _f (V) ^c	<i>E</i> _{p,a} (V) ^a	<i>E</i> _{p,c} (V) ^a	<i>E</i> _f (V) ^c	<i>i</i> _{p,a} / <i>i</i> _{p,c}
0.1 M LiClO ₄ /EtOH	Au	0.26	0.19	0.86	1.05	0.23	0.25	0.14	0.18	2.7
	Pt	0.27	0.21	0.99	0.96	0.24	0.26	0.17	0.21	1.7
	GC	0.28	0.19	0.67	1.15	0.23	0.24	0.16	0.20	2.0
0.1 M Bu ₄ NBF ₄ /MeCN	Au	0.28	0.20	0.75	1.12	0.24	–	–	–	–
	Pt	0.28	0.21	0.86	1.09	0.24	0.27	0.17	0.20	2.3
	GC	0.32	0.20	0.49	1.30	0.26	–	–	–	–
0.1 M Bu ₄ NBF ₄ /DCMe	Pt	0.27	0.21	0.96	1.02	0.24	0.28	0.16	0.22	1.9

^a*E*_{p,a}, *E*_{p,c} = anodic and cathodic peak potentials, respectively

^b*n* = number of electrons exchanged between ions ($n = \Delta E_p / 0.059$ V)

^c*E*_f = formal potential

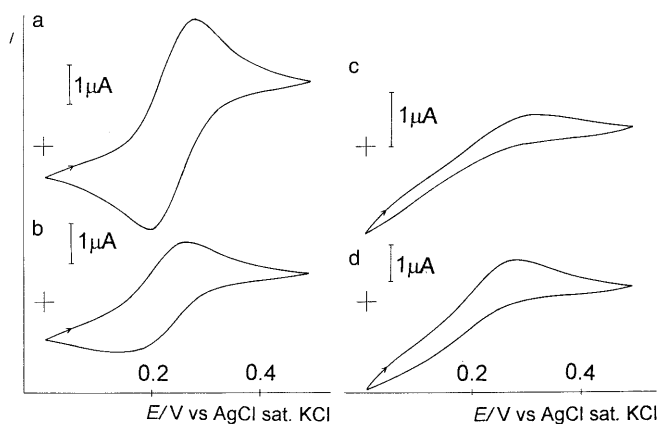


Fig. 1 Cyclic voltammograms (CVs) of 1.2 mM $[\text{Co}(-)\{\text{chxn}(\text{salal})_2\}]$, 0.1 M LiClO_4 , EtOH, Pt electrode: **a** initial CV (argon), **b** after bubbling oxygen through for 1 h, **c** after 24 h contact with oxygen, **d** as **c** but de-aerated after bubbling argon through for 1 h. Scan rate 0.1 V s^{-1}

without a cathodic response. This observation correlates with the slow kinetics of electron transfer in cobalt(II) species at an electrode surface, which is usually the case in the absence of coordinating axial ligands [25]. The shape of this voltammogram does not revert to the one in Fig. 1a, even after a large number of scans (Fig. 1d). We can assume that a new compound (oxygen adduct), electrochemically inactive in the 0.0–0.5 V potential range, has been formed. The increase in the anodic peak intensity after de-oxygenation of the electrolyte solution (Fig. 1d) can be explained by the partial decomposition of this adduct with Co(II) recovery.

The anodic and cathodic peak currents obtained after prolonged oxygenation of the solution, measured in argon after the shape of the CV had reached a steady state, are presented in Fig. 2. The gradual disappearance of the cathodic peak (curve b) and the position of the inflection point of the anodic one (curve a) suggest that the oxygenated form of the complex has been formed almost completely ($t \approx 60 \text{ min}$, EtOH, 0.1 M LiClO_4 , $[\text{Co}(-)\{\text{chxn}(\text{salal})_2\}] = 1.05 \text{ mM}$, 25°C). In MeCN solutions a longer time was required for equilibrium to be reached ($t \approx 3 \text{ h}$), probably because of the lower solubility of the complex in this solvent.

Oxygen reduction

Repeated CVs recorded between -0.90 V and 0.50 V (the first cycle started from 0 V , 0.8 mM $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$, 0.1 M LiClO_4 , EtOH, air) are shown in Fig. 3. Because there was no anodic response in the potential range between -0.90 and 0.0 V , only the cathodic sections of the CVs are reproduced (for clarity, the anodic sections of the second and subsequent curves have been omitted). The first cycle, recorded a few seconds after aeration of the electrolyte solution, shows two overlapping cathodic waves at -0.14 V and -0.32 V (Fig. 3,

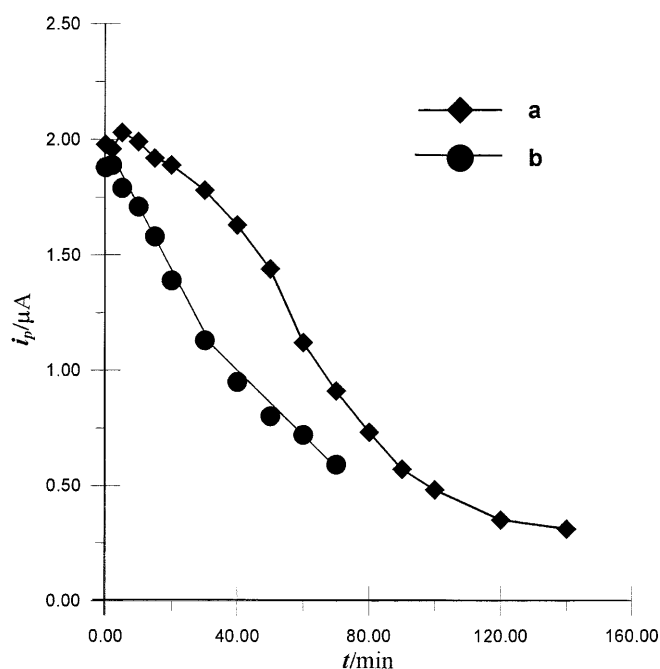


Fig. 2 Anodic (**a**) and cathodic (**b**) peak currents of a Co(III)/Co(II) couple as a function of oxygenation time (the solution is the same as in Fig. 1)

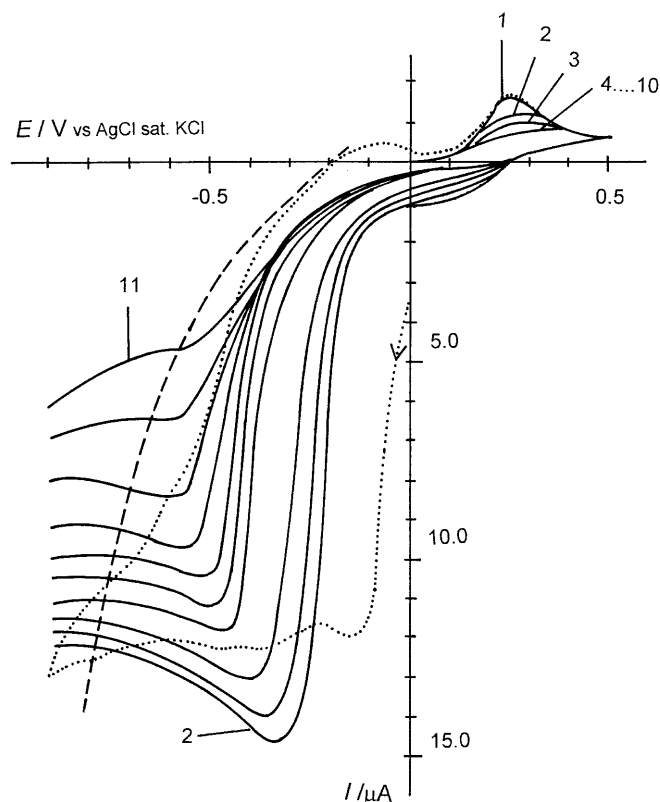
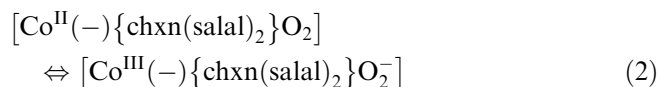
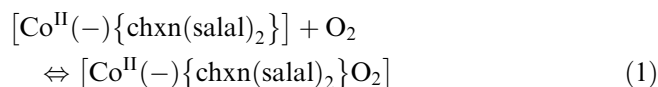


Fig. 3 Sections of CVs recorded with sweeps from 0.0 V to 0.5 V and then to -0.9 V for 0.8 mM $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$, 0.1 M LiClO_4 , EtOH, oxygen; dotted line: first cycle; dashed line: wave of O_2 reduction in the blank solution. Scan rate 0.1 V s^{-1}

dotted line). In the second and subsequent cycles (Fig. 3, solid line), the first maximum disappeared and only the one at the more negative potential was detected. Simultaneously, the peaks associated with the $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]/[\text{Co}^{\text{III}}(-)\{\text{chxn}(\text{salal})_2\}]^+$ couple (between 0.1 and 0.4 V) disappear gradually. These changes in the oxygen maximum suggest that two forms of oxygen are indeed formed in the complexes. These observations and literature data [3, 7] can be summarized by the following reactions:



Equation 2 shows a pair of mesomeric structures created as a result of intramolecular charge transfer. The first oxygen maximum found at $E_p = -0.14$ V can be assigned to the reduction of the Co(III) moiety in $[\text{Co}^{\text{III}}(-)\{\text{chxn}(\text{salal})_2\}\text{O}_2^-]$, the second one ($E_p = -0.32$ V) to the reduction of the activated dioxygen in $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}\text{O}_2]$ molecules. The observed positive shift of the oxygen wave (ca. 0.25 V) in relation to the reduction potential of the free O_2 ($E_p = -0.60$ V) (Fig. 3, dashed line) indicates the presence of an activated O_2 molecule linked with the Co(II). The lack of an anodic response in the potential range (from -0.9 to 0.0 V) indicates that reduced forms of oxygen do take part in chemical reactions following electron transfer.

Anodic oxidation

Several CVs (0.9 mM $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$, argon) recorded between 0.0 V and 1.2 V in MeCN are presented in Fig. 4. The first cycle exhibits the anodic peak characteristic of $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$ oxidation ($E_{p,a} = 0.26$ V), and is followed by the wave at 0.8–1.1 V. The lack of a cathodic response indicates that both processes are irreversible, which speaks for the low electrochemical activity of the oxidized species or the oxidative destruction of the catalyst [8]. In subsequent cycles the Co(II) oxidation peak vanishes, while a new anodic peak emerges in the 0.55–0.80 V range. Simultaneously, the magnitude of this peak increases up to the fifth scan, after which it begins to decrease in size. It is followed by a double anodic wave between 0.85 and 1.15 V, whereas the cathodic part revealed the presence of a broad reduction peak (max. 0.85 V). Wave potentials and the shape of the observed steady-state CV (Fig. 4, dotted line) are similar to the results obtained for various cobalt(II)-Schiff base complexes [12, 19, 26, 27].

It is noteworthy that at the end of measurements in MeCN, the platinum electrode was coated with a yellow layer. A similar phenomenon, related to electropoly-

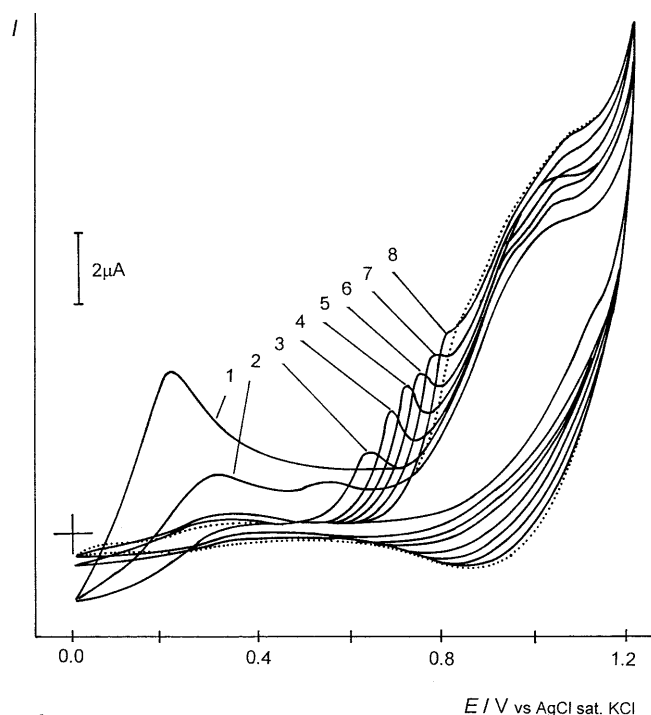


Fig. 4 Development of CVs in 1.1 mM $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$ MeCN, 0.1 M Bu_4NBF_4 (scans 1–8); dotted line: steady-state curve. Scan rate 0.1 V s^{-1}

merization [10, 11, 18, 19], was observed with the several metal-centered organic ligands such as porphyrin compounds, phthalocyanines and Schiff base compounds. The results of the XPS study of both the solid $[\text{Co}(-)\{\text{chxn}(\text{salal})_2\}]$ and the electrochemically prepared layer on the Pt electrode are shown in Fig. 5. Detailed analysis of the $[\text{Co}(-)\{\text{chxn}(\text{salal})_2\}]$ spectrum in the Co $2p_{3/2}$ region (Fig. 5a) revealed a resemblance to the literature results for Co(II)-Schiff base complexes [27]. The XPS spectrum of the electrochemically obtained layer exhibits a single, narrow Co $2p_{3/2}$ peak at 781 eV (Fig. 5b) assigned to the Co(III) (90%) species [21, 28, 29]. This layer thus appears to consist of the oxidized Co(III) species, which can react rapidly with each other forming a stacked acceptor-donor deposit [30, 31].

Electrochemical studies in the presence of 4-methyl-1-cyclohexene

CVs of the oxygen-saturated ethanolic solution of $[\text{Co}^{\text{II}}\{\text{chxn}(\text{salal})_2\}]$ (1 mL, 0.98 mM) were recorded 30 s after the addition of 50 μL of 4-methyl-1-cyclohexene (mchx) (Fig. 6, dashed line). The anodic part of the curve exhibits peaks at 0.72 and 0.90 V, which suggests that two successive oxidations take place. They can be assigned to the charge-transfer reactions of $[\text{Co}^{\text{III}}(-)\{\text{chxn}(\text{salal})_2\}\text{O}_2^-]$ in the μ -superoxo-/ μ -peroxo-dicobalt(III) couple. The reducing agent (mchx) present in the electrolyte solution prevents anodic polymerization of the complex and the electrode surface remains pure

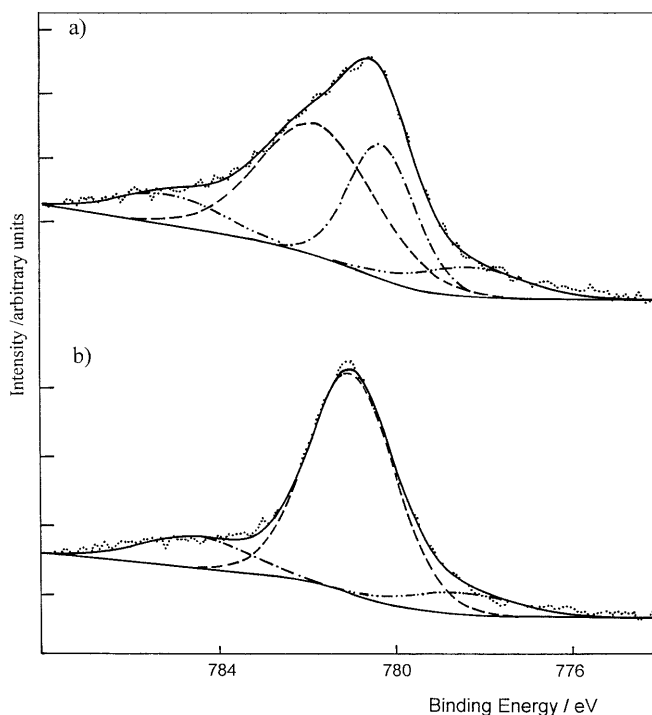


Fig. 5 Comparison of Co $2p_{3/2}$ XP spectra of cobalt species in solid $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$ and electrochemically deposited at a Pt electrode

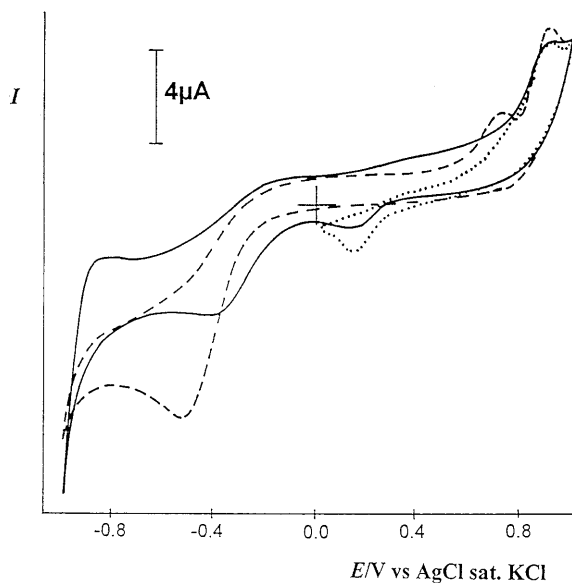
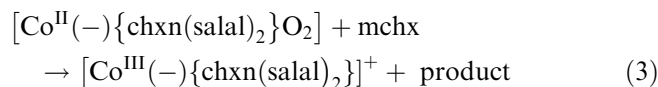


Fig. 6 CVs of 1.0 mM $[\text{Co}^{\text{II}}(-)\{\text{chxn}(\text{salal})_2\}]$, 0.1 M LiClO_4 , EtOH in the presence of 4-methyl-1-cyclohexene and oxygen; *solid line*: potential range from -0.9 V to 1.0 V (*dashed line*: first cycle); *dotted line*: potential range from 0.0 V to 1.0 V. Scan rate 0.1 V s^{-1}

during cyclization. The shape of the cathodic peak (-0.45 V) is characteristic of the catalytic reduction of oxygen in peroxide systems [3, 7, 8]. The CV shape became stable (Fig. 6, solid line) after repeated runs and a single anodic ($E_{\text{p,a}} = 0.92 \text{ V}$) as well as a cathodic peak ($E_{\text{p,c}} \approx 0.20 \text{ V}$) were observed. The superoxide moiety

oxidation ($\text{O}_2^- \rightarrow \text{O}_2 + \text{e}^-$) and reduction of Co(III) ($\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$) in $[\text{Co}^{\text{III}}(-)\{\text{chxn}(\text{salal})_2\}\text{O}_2^-]$ can be assigned to these peaks. The CV recorded within a narrower range of potentials (0.0–1.0 V) without cathodic reduction of oxygen (Fig. 6, dotted line) exhibits the same anodic ($E_{\text{p,a}} = 0.88 \text{ V}$) and cathodic ($E_{\text{p,c}} = 0.20 \text{ V}$) peaks. The shape of the CV stabilizes within 60 s and is limited by the changes in the system such as oxidation of the alkene, formation and decomposition of the oxygen adduct, reduction of Co(III) to Co(II), and oxidation of the oxygen species. The CV experiment in the potential range from 0.0 to 1.0 V for a complex-free solution yields only a background current; the above interpretation is confirmation of this. It is possible that in the first stage the dioxygen moieties (O_2 or/and O_2^-) oxidize the mchx until the entire Co(II) complex has been converted into the Co(III) species, according to the scheme:



The reactions reached a steady state after 5 min, and after 1 h no more changes in the shape of the CVs were recorded between 0.0 and 1.0 V (Fig. 6, dotted line). The appearance of the cathodic peak due to Co(III) reduction and the lack of an anodic response imply a rapid linkage of electrogenerated Co(II) with dissolved oxygen.

Aerobic oxidation of cycloalkenes

Cyclohexene and 4-methyl-1-cyclohexene were utilized as substrates and catalytically oxidized with air. Cyclohexene oxidizes in the presence of $[\text{Co}(-)\{\text{chxn}(\text{salal})_2\}]$ to a mixture of 2-cyclohexen-1-ol and 2-cyclohexen-1-one. During the reaction, the product distribution changed. After 8 h, 2-cyclohexen-1-ol ($\sim 7.5\%$), 2-cyclohexen-1-one ($\sim 29\%$) and cyclohexene (60%) were detected, while after 24 h the only product appeared to be 2-cyclohexen-1-one. Oxidation of 4-methyl-1-cyclohexene after 24 h gave a more complicated pattern, as indicated by the peaks from isomeric allylic α,β -ketones (67%) and alcohols (23%). These results suggest that α,β -allylic alcohols are less stable under the experimental conditions and, accordingly, selectivity is marginal. It is probable that, in the oxidation process, $[\text{Co}(-)\{\text{chxn}(\text{salal})_2\}]$ generates oxygen-bound species like the one shown in Eq. 2. The oxidation mechanism proposed by Valentine and co-workers [3] requires the reaction of high-valent oxo intermediates, able to react with the alkene in a fashion analogous to the previously observed reactions of peroxy acids with alkenes catalyzed by metal complexes. The catalytically active species proposed in our electrochemical system are oxygenated forms of cobalt(III) in which O_2 is bound in the superoxo or peroxy form. Evidence for this is the positive

shift (ca. 0.25 V) of the oxygen reduction potential in relation to the free O₂. An analogous mechanism was proposed for the oxidation of hydrocarbons by dioxygen catalyzed by the iron(III) salen complex [32, 33]. The first step is thus assumed to be oxygen transfer, which is followed by a radical-governed transformation. In this case the yield of the various products will vary with the substituents of the initial alkene and the solvent. Both we and others studying similar catalytic reactions appear to have reached the same conclusion [32, 33, 34, 35].

Conclusion

This study describes the electrochemical behavior of a freshly prepared [20] cobalt-Schiff base complex and its catalytic activity in oxidation processes. The data presented provide some evidence for the interaction of O₂ with the complex. While we have not identified the adduct directly, it seems reasonable for the observed catalytic effects to be described by the presence of an active form of oxygen. Anodic electropolymerization of the complex forms a solid material with dominant Co(III) species on the electrode.

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