CROATICA CHEMICA ACTA CCACAA **75** (1) 165–173 (2002)

ISSN-0011-1643
CCA-2790 *Original Scientific Paper*

Binding of Molecular Dioxygen to the Cobalt(II) Complexes in Nonaqueous Solution

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Recieved July 24, 2000; revised November 7, 2001; accepted November 14, 2001

The study discusses the possible binding of molecular oxygen to some new Co^{II} complexes with the Schiff base ligands of the Co(Salen) type. The investigated complexes of Co^{II} with the Schiff bases are: (bis(5-nitro-salicylaldehyde)ethylenediaminato)cobalt(II), Co(NSalen); (bis(α-ethylene-salicylaldehyde)ethylenediaminato)cobalt(II), Co(EtSalen); (bis(α-ethylene-3,5-diiode-salicylaldehyde)ethylenediaminato)cobalt(II), Co(DIEtSalen); (bis(α,5-dimethyl-3-iode-salicylaldehyde)ethylenediaminato)cobalt(II), Co(DMISalen) and (bis(salicylaldehyde)methylene-*p,p'*-diphenylenediaminato)cobalt(II), Co(Salmbfn). The studies were based on cyclic voltammetry and UV-Vis spectrometry, in DMF solution. Electron-withdrawing substituents on the Schiff bases were found to decrease the affinity of the cobalt Schiff bases for dioxygen. Equilibrium dioxygen uptake measurements over a large range of temperatures provide the ΔH° and ΔS° values of oxygenation that fall in the range –37 to –50 kJ mol^{-1} for ΔH° and –117 to –157 J mol^{-1} K^{-1} for ΔS°, which is in line with the values reported for analogous dioxygen complexes described in literature.

Key words: cobalt(II) complexes, dioxygen binding, Schiff bases.

INTRODUCTION

The ability of the Co^{II} complexes to bind molecular dioxygen has been known for quite a long time.[1] In the last decades, the specialists' attention has been focused on this aspect with the aim to some synthetic carriers of oxygen that should mimic the natural biological systems in fixation, release,

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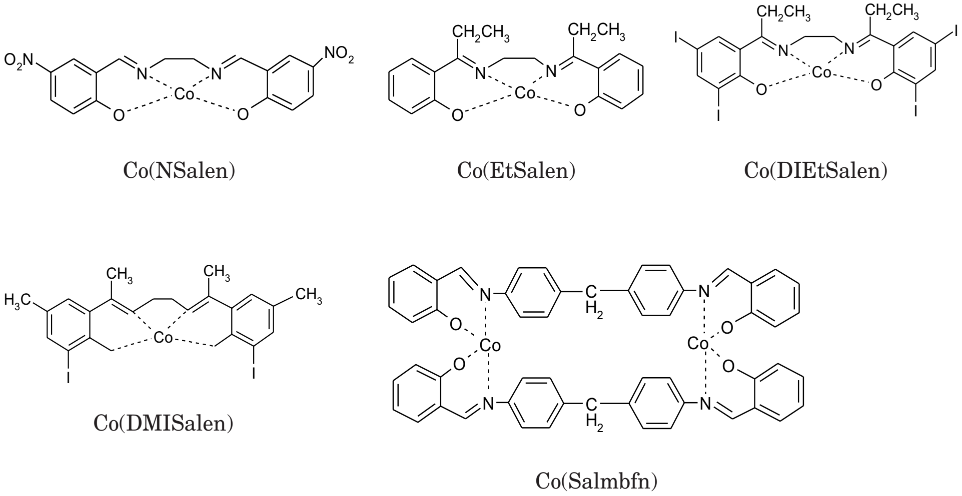
stocking and activation of dioxygen.[2,3] The complexes' behaviour depends on their physical state. Thus, in the solid state, they may evidence spontaneous activity towards dioxygen, but only after a preliminary activation phase.[4] In solution, in donor organic solvents, several complexes manifest activity toward O_2 in a spontaneous manner. Interesting studies on this issue have been elaborated by Basolo, Martell, Pâris, *etc*.[5–7] Most of them were performed on octahedral chelates of the bis(salicylaldehyde)ethylenediimine)-cobalt(II) type, Co(Salen), known to possess two potentially vacant axial positions. For O_2 fixation, the presence of a base or a sufficient donor solvent is necessary, in order to occupy one of the axial positions, the other permitting reversible binding dioxygen.[8] Studies performed in an aqueous solution – with a higher degree of difficulty – depend equally on the nature of the ligands and complexes, on pH, *etc*.[9]

The present paper analyzes dioxygen binding, as performed by Co^{II} complexes with the Schiff bases, by cyclic voltammetry and UV-Vis spectroscopy, in dimetylformamide (DMF) solutions. The structures of the used complexes are presented in Figure 1.



Co(NSalen) Co(EtSalen) Co(DIEtSalen)

Co(DMISalen) Co(Salmbfn)

Figure 1. Structures of the cobalt(II) complexes.

The Co^{II} complexes with the Schiff bases are: (bis(5-nitro-salicylaldehyde)-ethylenediaminato)cobalt(II), Co(NSalen); (bis(α-ethylene-salicylaldehyde)-ethylenediaminato)cobalt(II), Co(EtSalen); (bis(α-ethylene-3,5-diiode-salicylaldehyde)ethylenediaminato)cobalt(II), Co(DIEtSalen); (bis(α,5-dimethyl-3-iode-salicylaldehyde)ethylenediaminato)cobalt(II), Co(DMISalen) and (bis-(salicylaldehyde)methylene-*p,p'*-diphenylenediaminato)cobalt(II), Co(Salmbfn).

EXPERIMENTAL

The synthesis of coordinative compounds was done by the Bailles and Calvin method.[10] They were characterized by elemental analysis, UV-Vis and IR spectroscopy, X-ray diffraction and cyclic voltammetry.[11]

Cyclic voltammetry was developed on a PAR 263 A voltammeter, operated by a computer, which employed the PAR 270 M software. The recordings were made on a solution with a concentration of 2 mmol dm^{-3}, in DMF, using 0.1 mol dm^{-3} $LiClO_4$, as a supporting electrode. The working electrode was vitreous carbon, with the electroactive area A = 3.8 mm^2. Saturated Ag/AgCl was used as a reference and a platinum wire as an auxiliary electrode. Cyclic voltamograms of the complexes' solution, prepared under an argon atmosphere in anhydrous and degassed DMF, were recorded. Then, the oxygen was bubbled for 3–5 min in solution. The excess of O_2 from the solution was removed through bubbling of Ar (for 5–10 min), and the cyclic voltamograms were recorded. Then an efficient bubbling of Ar followed for 20–30 min, accompanied by stirring of the solution to remove O_2 from the complex, and the cyclic voltamograms were recorded once more.

The qualitative and quantitative determinations of O_2 binding were performed by UV-Vis spectroscopy. The comparative UV-Vis spectra of the complexes and adducts were obtained in DMF solution on a double ray DES device, equipped with a computer, using the Safas for Windows 95 software. Determinations were made in DMF solution, at an optimum concentration of pyridine (previously determined) and at temperatures ranging between 1–45 °C.

RESULTS AND DISCUSSION

In cyclic voltammetry, the complexes – with the exception of Co(Salmbfn) – exhibit a quasi-reversible behaviour. The presence of pyridine in the complex solution in DMF (c_{py} ranging between 55–95%), leads to the formation of the [CoL(DMF)(py)] compound, characterized by lower values of the redox potentials compared to the initial complex.[12] Cyclic voltamograms of the solution of complexes indicate significant modifications, both in the absence and in the presence of O_2, Figure 2.

The reaction that most probably occurs in the presence of O_2 is:

$$[\mathrm{Co^{II}L(DMF)(py)}] + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{III}L(py)(O_2)}] + \mathrm{DMF} \qquad (1)$$

In the absence of O_2, the complex is stable, evidencing a quasi-reversible behaviour (Figure 2, curve 1). The adduct formed in the presence of O_2 is very unstable, while the Co^{III} complex subjected to reduction through cyclic voltammetry (Figure 2 curve 2) is very quickly reoxidated to the Co^{III} complex, which is much more stable.[13] If O_2 is reversibly bound to the Co complex, the former should be eliminated, and the complex should exhibit the same behaviour as the initial one (Figure 2 curve 3). In the case of the

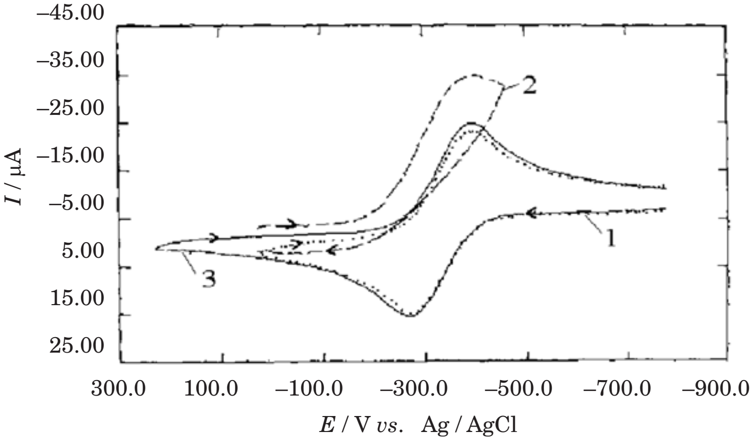


Figure 2. Cyclic voltamograms of the Co(DMISalen) complex; 1 – solution prepared initially in inert atmosphere; 2 – complex in the presence of O_2; 3 – complex after O_2 elimination, c_{CoL} = 0.2 mmol dm^{-3}, c_{py} = 0.2 mol dm^{-3}, v = 0.1 V s^{-1}.

Co(DMISalen) complex, one may observe that the cyclic voltamograms, for both the initial form and the one after O_2 elimination, are almost identical, which indicates binding of O_2 by this complex. Similar behaviour has been recorded for all Co^{II} complexes, evidencing a reversible or quasi-reversible behaviour in cyclic voltammetry, while the Co(Salmbfn) complex shows an irreversible behaviour in cyclic voltammetry.

UV-Vis spectroscopy shows oxygen's qualitative and quantitative fixation. Bubbling of oxygen, at various partial pressures and temperatures, through the complex solution, enables to observe an increase of the values of absorbants (Figure 3).

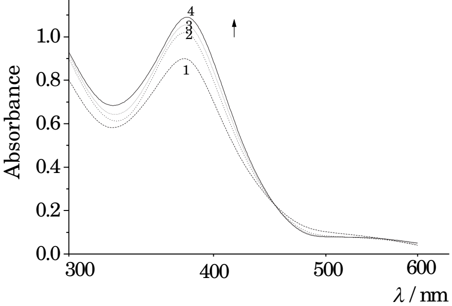


Figure 3. Evolution of absorbance in O_2 bubbling in the Co(DMISalen) complex; $c_{\mathrm{CoL}} = 10^{-4}$ mol dm^{-3}, T = 286 K, 1 – initial, 2,3 – in the presence of oxygen (air), 4 – in the presence of pure oxygen.

With the increase of the partial pressure of O_2, the value of absorbance also increases, up to a value that is maintained constant. Bubbling of an inert gas, accompanied eventually by heating of the solution, leads to a reduction of absorbance, as compared with the initial one. New oxygen bubbling leads again to an increase of absorbance, a second oxygenation cycle being thus realized. Figure 4 represents the two oxygenation cycles for the [Co(DIEtSalen)] complex. The DMF concentration is considered approximately constant, having no influence on the complex concentration.

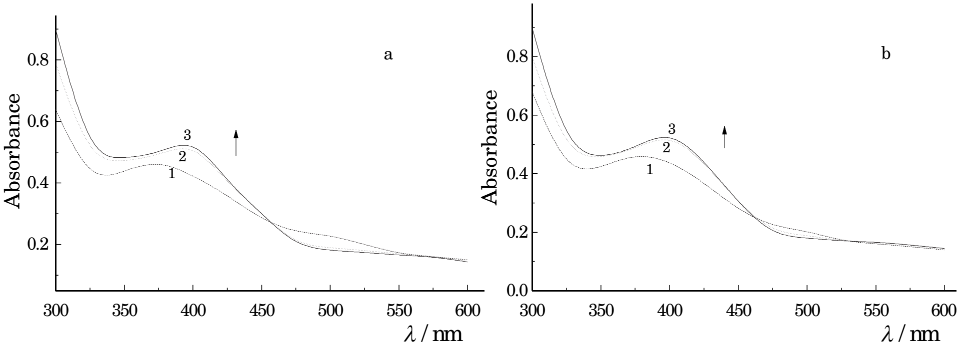


Figure 4. The first two cycles (a and b) of oxygenation for the Co(DIEtSalen) complex, $c_{\text{CoL}} = 10^{-4}$ mol dm^{-3}, T = 274 K, 1 – initial, 2 – in the presence of oxygen (air), 3 – in the presence of pure oxygen.

The oxygenation constant, corresponding to reaction (1), is defined according to relation (2), where B is an axial ligand, *e.g.*, py or DMF:[14,15]

$$K_{O_2} = \frac{[\text{LCoBO}_2]}{[\text{LCoB}] \cdot P_{O_2}} \tag{2}$$

If, at the wave length considered in the study, the only absorbing species are [LCoB] and [LCoBO$_2$], one may calculate the oxygenation constant, K_{O_2}, as a function of absorbance modifications of the present species, by applying Eq. (3).[6]

$$K_{O_2} = \frac{A - A_0}{A_t - A} \cdot \frac{1}{P_{O_2}} \tag{3}$$

where: A_0 – initial absorbance,
A_t – total absorbance,
A – absorbance at various oxygen pressure values,
P_{O_2} – oxygen pressure during semi-oxygenation.

The oxygenation constants determined using relation (3), at different working temperatures, are listed in Table I. If the experimental values of K_{O_2}, at different temperatures, obey the van't Hoff equation, then the thermodynamic parameters may be determined from the graph of function (4), Figure 5,

$$\ln K_{O_2} = f(1/T) \tag{4}$$

with relation (5)

$$\ln K_{O_2} = -(\Delta H^\circ / RT) + (\Delta S^\circ / R) \tag{5}$$

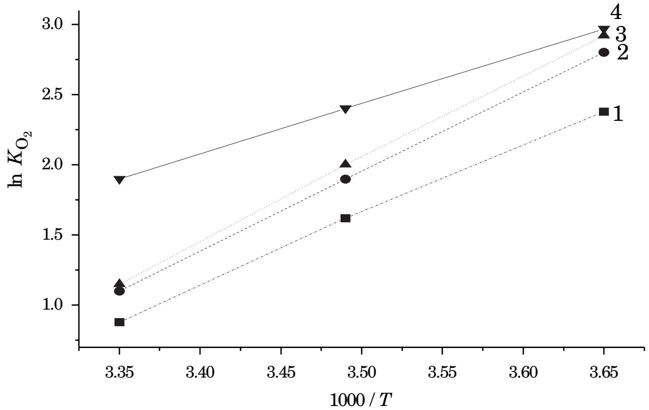


Figure 5. Van't Hoff diagrams for the complexes: 1 – Co(NSalen), 2 – Co(EtSalen), 3 – Co(DIEtSalen), 4 – Co(DMISalen).

The data given in Table I show the decrease of the oxygenation constants with the increase of temperature. They are correlated with the values of the halfwave potentials corresponding to the complexes. The higher is the halfwave potential $E_{1/2}$, corresponding to the lower oxygenation constants, K_{O_2}, (Table II) the corresponding complex resist a larger number of oxygenation-deoxygenation cycles.

This correlation may be related to the nature of the substituents grafted on ligands. The presence of some ligands possessing ($-NO_2$) attracting effects induces a decrease in the density of the electrical charge on the central ion, which will result in its more difficult oxidation to more reduced potentials. The presence of some relatively bulky groups correlated with the presence of some electron-attracting substituents on ligands ($-CH_3$, $-CH_2-CH_3$) protects the central ion, so that it may participate in a higher number of oxygenation-deoxygenation cycles. The Co(NSalen) complex resists at least

TABLE I

Values of the oxygenation constant and of the thermodynamic parameters for the CoL complexes

Complex	c / mmol dm^{-3}	c_{py} / mol dm^{-3}	T / K	K_{O_2} / atm^{-1}	ΔH° / kJ mol^{-1}	ΔS° / J mol^{-1} K^{-1}
Co(NSalen)	0.1	0.01	274	10.52	–37.56	–117.5
Co(NSalen)	0.1	0.01	286	5.20		
Co(NSalen)	0.1	0.01	298	2.43		
Co(NSalen)	0.1	0.01	318	1.08		
Co(EtSalen)	0.2	0.02	274	16.5	–49.66	–156.7
Co(EtSalen)	0.2	0.02	286	8.75		
Co(EtSalen)	0.2	0.02	298	2.96		
Co(DIEtSalen)	0.1	0.01	274	18.5	–46.50	–131.7
Co(DIEtSalen)	0.1	0.01	286	7.40		
Co(DIEtSalen)	0.1	0.01	298	3.05		
Co(DMISalen)	0.2	0.02	274	17.36	–45.2	–129.8
Co(DMISalen)	0.2	0.02	286	12.2		
Co(DMISalen)	0.2	0.02	298	6.75		

TABLE II

Correlation between the halfwave potentials, $E_{1/2}$, and the oxygenation constant, K_{O_2} (T = 286 K)

Compound	$E_{1/2}$ / V	K_{O_2} / atm^{-1}
Co(NSalen)	–0.52	5.20
Co(DIEtSalen)	–0.82	7.40
Co(EtSalen)	–0.88	8.75
Co(DMIsalen)	–0.93	12.20

10 cycles of this type, Co(DMISalen) at least 7, and the others at least 5 such cycles. The Co(Salmbfn) complex cannot bind O_2 in a reversible manner.

CONCLUSIONS

The complexes of Co^{II} with tetradentate Schiff bases bind the molecular oxygen reversibly, with the highest efficiency in the presence of aminic base which, in solution, occupies one of the axial positions of the Co^{II} complex and favours substitution of the other solvent molecule with O_2. Removal of O_2 may be effected by efficient bubbling of inert gas, which may be accompanied by heating of the solution. The cyclic voltammetry of the initial complex (non-oxygenated, oxygenated and deoxygenated), reveals such modifications. Spectrophotometric studies confirm reversible binding of oxygen. From the K_{O_2} variation with temperature one may determine the values of the thermodynamic parameters of oxygenation. They are correlated with the oxygenation constants and with the values provided by the oxygenation cycles, depending on the values of the semiwave potentials, on the nature of the substituents on ligands and on the steric hindrance effects.

Acknowledgment. – I thank Professor Irène Morgenstern-Badarau and Aurora Gref of the Paris-Sud University for their assistance with the electrochemical equipment and for helpful discussions.

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SAŽETAK

Vezivanje molekula kisika na komplekse kobalta(II) u nevodenim otopinama

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Istraživani su slijedeći kompleksi kobalta(II) sa Schiffovim bazama: (bis(5-nitrosalicilaldehid)etilendiaminato)kobalt(II), Co(NSalen); (bis(α-etilensalicilaldehid)etilendiaminato)kobalt(II), Co(EtSalen); (bis(α-etilen-3,5-dijodo-salicilaldehid)etilendiaminato)kobalt(II), Co(DIEtSalen); (bis(α,5-dimetil-3-jodo-salicilaldehid)etilendiaminato)kobalt(II), Co(DMIsalen) i (bis(salicilaldehid)metilen-*p*,*p*-difenilendiaminato)kobalt(II), Co(Salmbfn). Istraživanja su provedena metodama cikličke voltammetrije i UV-Vis spektroskopije, za što su ispitivani uzorci bili otopljeni u dimetilformamidu. Nađeno je da afinitet kompleksa Schiffovih baza s kobaltom prema molekulama kisika opada s porastom sposobnosti supstituenata u Schiffovim bazama da odvlače elektrone. Ravnotežna mjerenja vezivanja kisika na proučavanim kompleksima preko širokog temperaturnog područja utvrdila su da ΔH° ima raspon vrijednosti od 37 do 50 kJ mol^{-1}, a ΔS° od 117 do 157 J mol^{-1} K^{-1}, što je u skladu s literaturnim vrijednostima vezivanja kisika na srodnim kompleksima.