Cobalt(II) Complexes with Substituted Salen-Type Ligands and Their Dioxygen Affinity in *N*,*N*-Dimethylformamide at Various Temperatures

Andreas Huber,[a] Lutz Müller,[a] Horst Elias,*[a] Robert Klement,[b] and Marian Valko[c]

Keywords: Cobalt / Oxygen / Schiff bases / Substituent effects / Thermodynamics

Several unsymmetrically substituted salen-type cobalt(II) Schiff-base complexes CoL [H_2L = 1,6-bis(2-hydroxyphenyl)-3,3-dimethyl-2,5-diaza-1,5-hexadiene (**1**); 1,6-bis(2-hydroxyphenyl)-3,3-dimethyl-2,5-diaza-1,5-heptadiene (**2**); 1-(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-6-(2-hydroxyphenyl)-3,3-dimethyl-2,5-diaza-1,5-heptadiene (**3**); 1-(2-hydroxyphenyl)-6-methyl-2,5-diaza-1,5-nonadien-8-one (**4**); 1-(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-6-methyl-2,5-diaza-1,5-nonadien-8-one (**5**); 1-(2-hydroxyphenyl)-3,3,6-trimethyl-2,5-diaza-1,5-nonadien-8-one (**6**); 1-(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-3,3,6-trimethyl-2,5-diaza-1,5-nonadien-8-one (**7**)] were prepared and characterized by their UV/Vis absorption spectra, magnetic moments, and oxidation potentials. Except for complex **4** (irreversible oxidation with $t_{½} \approx 3$ h), complexes **1**–**3** and **5**–**7** are remarkably resistant against irreversible auto-oxidation in air-saturated *N*,*N*-dimethylformamide (DMF) at ambient temperature. To characterize the Lewis acidity of the cobalt center in **1**–**7**, the equilibrium constant K_{py} was determined for monoadduct formation with pyridine (CoL + py ⇌ CoL·py). An O_2-sensitive optode was used to determine the Henry constant, K_H, for the system O_2/DMF in the temperature range 298–228 K. The formation of 1:1 adducts of complexes **1**–**7** with O_2 in DMF, as characterized by the equilibrium constant K_{O_2}, was followed spectrophotometrically in the temperature range 298–228 K. The parameters ΔH^o, ΔS^o, and K_{O_2} are reported. At 298 K, K_{O_2} ranges from 21.9 M^{-1} (**5**) to 155 M^{-1} (**7**). The overall spectroscopic information, including EPR spectra obtained with frozen solutions of **3** and **7** in O_2-saturated DMF, confirm that the 1:1 adducts CoL·O_2 are cobalt(III) superoxo compounds. The symmetrically substituted salen complex **8** [H_2L = 1,6-bis(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-3,3,4,4-tetramethyl-2,5-diaza-1,5-hexadiene in **8**] is shown to catalyze the oxidation of triphenylphosphane and 2,6-di-*tert*-butylphenol by O_2 in DMF at ambient temperature. The correlation of the data obtained for K_{O_2}, K_{py}, and the oxidation potential $E_{½}$ is discussed.

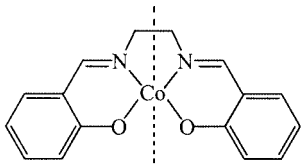
Introduction

In 1938 Tsumakis discovered the reversible binding of dioxygen to the cobalt(II) complex Co(salen).[1] Since then there has been a continuous and increasing interest in this complex and its derivatives as well as in other dioxygen-binding Schiff-base cobalt(II) complexes such as Co(acacen) and Cobaloxime. This interest arises from the potential application of these compounds as solids for the storage of dioxygen and for dioxygen-separation processes.[2,3] Furthermore, solutions of these complexes have been widely studied as dioxygen carriers and as catalysts for oxidation processes under mild conditions.[2] Martell and coworkers have prepared a number of derivatives of Co(salen) by introducing substituents in the 3- and/or 5-position of the aromatic rings of the ligand salen and by modifying the CH_2-CH_2 bridge connecting the two nitrogen donor atoms.[3,4] They investigated the formation of dioxygen adducts in systems CoL/O_2/B (CoL = salen-type Co^{II} complex; B = base) in solution at various temperatures and reported the corresponding equilibrium constants K_{O_2} and how they are affected by the nature of the base B coordinated to the cobalt center in the axial position. Busch and coworkers have prepared and studied O_2-binding cobalt(II) complexes with pentadentate salen-type ligands offering a (O∩N)∩N∩(N∩O) set of donor atoms, with the central N atom occupying an axial position at the cobalt center as an internal base.[5]

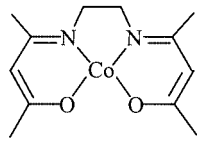
Co(salen) and Co(acacen) can be classified as four-coordinate chelate Co^{II} complexes with an N_2O_2 set of donor atoms. As shown by the cobaloximes[6] and by Co^{II} complexes with N_4 macrocyclic ligands[7] or with aliphatic N_x and N/O chelate ligands,[8,9] an affinity of the cobalt center for dioxygen is also generated by planar N_4 donor systems. For all the O_2-binding complexes CoL, where L is an N_2O_2- or N_4-type ligand, it is generally found that the interaction

[a] Eduard Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt,
Petersenstrasse 18, 64287 Darmstadt, Germany
Fax: +49-6151-166040
E-mail: elias@ac.chemie.tu-darmstadt.de
[b] VILA Center, University of Alexander Dubček Trenčín, Študentská 2, 911 50 Trenčín, Slovakia
[c] Faculty of Chemical and Food Technology, Slovak Technical University,
812 37 Bratislava, Slovakia

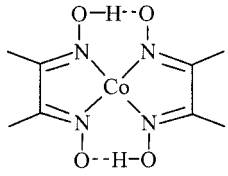
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Co(salen) ("Salcomine")



Co(acacen)



Cobaloxime

of the cobalt with dioxygen is more or less favored by an additional base B (such as pyridine, for example) coordinated in one of the axial positions to form five-coordinate CoL·B.

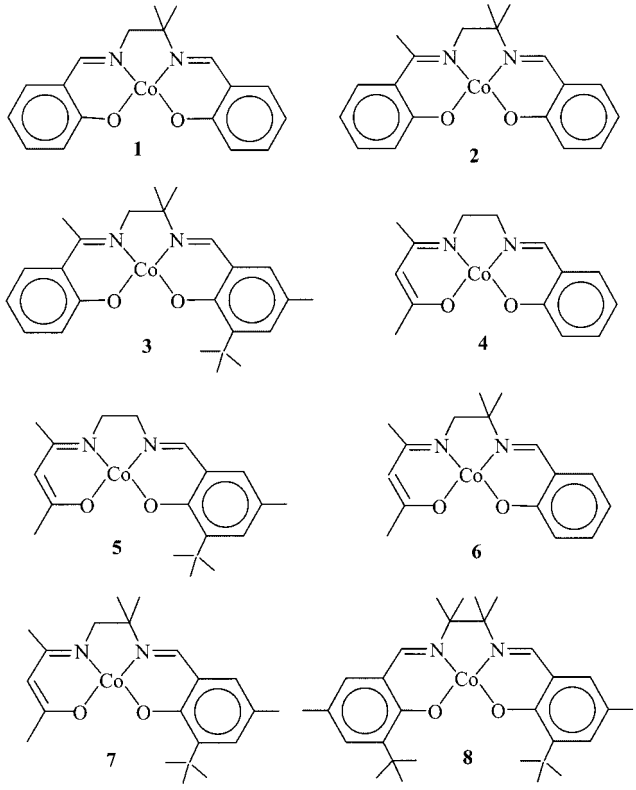
The ligand salen can be easily modified by the introduction of electron-releasing or electron-withdrawing substituents and sterically demanding groups. The electronic and steric properties of a given set of substituents on modified ligands salen* can drastically effect the electron density at the cobalt in Co(salen*) as well as the accessibility of the axial positions. An aerated solution of Co(salen), for example, is irreversibly auto-oxidized within hours. We found that, in contrast to Co(salen), an aerated solution of the cobalt salen complex **8**, which contains a number of methyl and *tert*-butyl groups (see Scheme 1), is stable for weeks. Nevertheless, complex **8** is a weak catalyst for oxidation reactions with O_2 (see Results and Discussion section).

The ligand salen is "symmetric" in the sense that it consists of two identical halves, as indicated by the dashed line in the structural formula of Co(salen) shown above. This sort of ligand symmetry is also typical for most of the derivatives of Co(salen) reported so far.[3,4] To provide a finer tool for property tuning, we decided to prepare a number of salen-type Co^{II} complexes **1**–**7** with "unsymmetric" ligands and to determine the corresponding equilibrium constants K_{O_2}. Compared to Co(salen), the two halves of the ligands in complexes **1**–**7** are no longer identical.

The present contribution summarizes the results obtained by investigating the effect of the various ligands in complexes **1**–**7** on the dioxygen affinity of the complexes in DMF at various temperatures, as characterized by equilibrium constants K_{O_2} according to Equation (1), on the Lewis acidity of the cobalt center, as characterized by equilibrium constants K_{py} according to Equation (2), and on the oxidation potential, $E_{1/2}$, of complexes **1**–**7**, according to the reaction $Co^{II}L \rightleftharpoons Co^{III}L^+ + e^-$.

$$CoL + O_2 \overset{K_{O_2}}{\rightleftharpoons} CoL{\cdot}O_2 \quad (1)$$

$$CoL + py \overset{K_{py}}{\rightleftharpoons} CoL{\cdot}py \quad (2)$$



Scheme 1. Structural formulae of the cobalt(II) complexes.

Results and Discussion

Preparation and Properties of the Complexes

Compared to salen and "symmetrically" substituted salen ligands such as the one in complex **8**, the synthesis of "unsymmetric" salen-type ligands is not at all simple. The ligands for the preparation of complexes **2**–**7** were obtained according to an efficient two-step procedure developed earlier.[10] On the basis of the known structure of complexes **3**[10] and **8**[11] one can extrapolate that, in all of the complexes **1**–**8**, the CoN_2O_2 core is nearly planar, with the plane of at least one of the two phenyl rings in **1**–**3** being almost co-planar with the CoN_2O_2 core. The UV/Vis spectra of complexes **1**–**8** are characterized by two intense charge-transfer (CT) bands at approximately 360 nm and 420 nm and by a weak d-d absorption (shoulder) at approximately 500 nm (see Table S1). The absorptivities of complexes **4**–**7** are smaller due to reduced conjugation. The magnetic moments of complexes **1**–**8** at 298 K were found to lie in the range μ_{exp} = 2.31–2.60 μ_B,[11,12] which is typically observed for low-spin d^7 systems of the present type.[13]

Auto-Oxidation of the Complexes in Solution

In air-saturated DMF solution at ambient temperature, the stability of complexes **1**–**8** towards irreversible auto-oxidation can be described by the following order: **8** > **1**–**3** > **5**–**7** > **4**. More specifically, a solution of complex **8** is stable for weeks and the solutions of **1**–**3** are stable for several

days, whereas those of complexes **5**–**7** change slowly within 24 h (<10%). Complex **4**, the least stable one, undergoes irreversible oxidative decomposition with a $t_{½}$ of about 3 h, which is close to the auto-oxidation rate of the parent complex Co(salen) in air-saturated DMF solution in the absence of bases such as pyridine.[14] One should note, however, that at –40 °C, adduct formation with dioxygen according to Equation (1) was shown to be reversible for all of the complexes **1**–**8**.

Potentials for the Oxidation Step $Co^{II} \rightarrow Co^{III}$

The data obtained for the potential $E_{½}$ in acetonitrile, which describes the quasi-reversible step $Co^{II} \rightarrow Co^{III}$, range from 183 to 274 mV (Table 1). The potential reported for unsubstituted Co(salen) in acetonitrile (258 mV)[15a,15b] lies within this range.

Table 1. Oxidation potentials, $E_{½}$, for complexes **1**–**8** in acetonitrile at 293 K.[a]

Complex	$E_{½}$ [mV][b]	Complex	$E_{½}$ [mV][b]
1	263	**6**	234
2	210	**7**	223
3	183	**8**	274
4	196	Co(salen)	258[c]
5	193	Co(salen)[d]	–33[e]

[a] $E_{½}$ referenced to SCE. [b] The peak separation, $E_p^c - E_p^a$, was in the range 82–144 mV. [c] The value presented is based on $E_{½}$ = –195 mV, as reported for acetonitrile and referenced to Fc/Fc^+ (Fc = ferrocene);[15a] conversion to SCE was achieved according to: $E(SCE) = E(Fc/Fc^+) + 453$ mV.[15b] [d] Solvent DMF. [e] The value presented is based on $E_{½}$ = –466 mV, as reported for DMF and referenced to Fc/Fc^+ (Fc = ferrocene);[15c] conversion to SCE was achieved according to: $E(SCE) = E(Fc/Fc^+) + 433$ mV.[15b]

The qualitative order of stability towards auto-oxidation (**8** > **1**–**3** > **5**–**7** > **4**), as obtained by spectrophotometric monitoring, does not correlate with the parameter $E_{½}$. The most positive oxidation potential (274 mV) is indeed found for the most stable complex **8**, but within the group of complexes **1**–**3**, which show the same sort of stability, the potential drops by 80 mV from 263 mV (**1**) to 183 mV (**3**). Moreover, within the group of complexes **4**–**7** complex **5** is found to be as stable as complexes **6** and **7**, but the potential of **5** (193 mV) is as low as **4** (196 mV), which is the least stable complex. As pointed out above, the instability of **4** resembles that of Co(salen), although the potentials differ by 64 mV.

The lack of a correlation between $E_{½}$ and the observed complex stability is not unexpected. The parameter $E_{½}$ is a measure of the energy needed to abstract an electron from the cobalt. The observed stability towards irreversible auto-oxidation, however, reflects a multi-step process that is probably initiated by docking of the O_2 molecule at the cobalt, followed by electron transfer from the cobalt to O_2, and followed by a further series of reactions that lead finally to the destruction of the complex. All of these steps can be subject to electronic and steric substituent effects in a specific way.

Adduct Formation with Pyridine

The cobalt center in complexes **1**–**8** is weakly Lewis acidic. As an example, Figure 1 shows the spectral changes associated with the stepwise titration of complex **3** with pyridine in toluene. The (A,[py]) data follow the relationship in Equation (6), which describes monoadduct formation according to Equation (2). The occurrence of a sharp isosbestic point indicates that there is no additional diadduct formation. The data obtained for the equilibrium constant K_{py} range from 6.3 M^{-1} for **1** to 0.3 M^{-1} for **7** (Table 2).

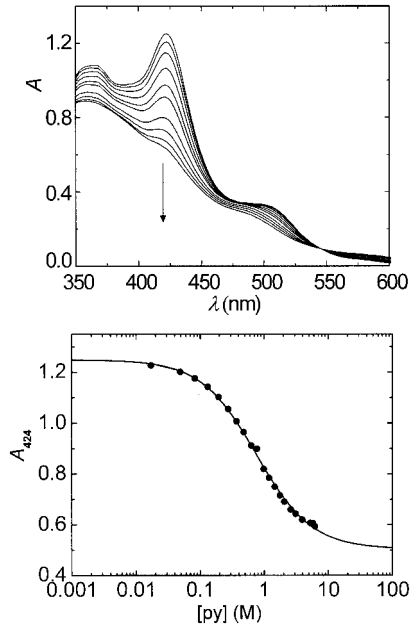


Figure 1. Spectral changes and titration curve describing the stepwise titration of complex **3** with pyridine in toluene at 298 K [solid line obtained by fitting Equation (6) to the (A_{424},[py]) data].

Table 2. Equilibrium constants, K_{py}, for adduct formation of complexes **1**–**8** with pyridine in toluene according to Equation (2) at 298 K.

Complex	K_{py} [M^{-1}]	Complex	K_{py} [M^{-1}]
1	6.3 ± 0.7	**5**	0.50 ± 0.01
2	3.0 ± 0.3	**6**	0.55 ± 0.10
3	1.3 ± 0.1	**7**	0.32 ± 0.01
4	1.3 ± 0.2	**8**	0.47 ± 0.01; 0.06 ± 0.01[a]

[a] The solvent was DMF instead of toluene.

For comparison of the K_{py} data, complexes **1**–**8** should be divided into two groups: in group **A** (complexes **1**–**3** and **8**), the ligand skeleton is that of salen, whereas in group **B** (complexes **4**–**7**) one half of the ligand is based on acetylacetone instead of salicylaldehyde. The fact that $K_{py}(\mathbf{1}) > K_{py}(\mathbf{6})$ reflects clearly that, independent of additional substituent effects, the acetylacetone-containing ligand system of complexes **4**–**7** is a stronger electron donor than that of salen.

In more detail, the analysis of the K_{py} data leads to the following conclusions: (i) the order observed for group **A** complexes, $K_{py}(\mathbf{1}) > K_{py}(\mathbf{2}) > K_{py}(\mathbf{3}) > K_{py}(\mathbf{8})$, reflects the combined electronic and steric effects of an increasing

number of methyl and *tert*-butyl groups, respectively, which increase the electron density and decrease the accessibility of the cobalt center; (ii) the order observed for group **B** complexes, $K_{py}(\mathbf{4}) > K_{py}(\mathbf{5}) \approx K_{py}(\mathbf{6}) > K_{py}(\mathbf{7})$, is due to the same sort of effects; (iii) the finding that $K_{py}(\mathbf{4}) > K_{py}(\mathbf{6})$ and $K_{py}(\mathbf{5}) > K_{py}(\mathbf{7})$ demonstrates the (probable) steric effect of two methyl groups on the CH_2-$C(CH_3)_2$ bridge of **6** and **7**, which reduce the accessibility of the cobalt; and (iv) the finding that $K_{py}(\mathbf{2}) > K_{py}(\mathbf{3})$, $K_{py}(\mathbf{4}) > K_{py}(\mathbf{5})$, and $K_{py}(\mathbf{6}) > K_{py}(\mathbf{7})$ can be ascribed to the combined electronic and steric substituent effects of the methyl group and *tert*-butyl group, respectively, in the *para*- and *ortho*-position to the phenolic oxygen.

For complex **8**, the addition of pyridine was measured in toluene (K_{py} = 0.47 M^{-1}) as well as in DMF (K_{py} = 0.06 M^{-1}). The apparently lower Lewis acidity in DMF confirms that, in DMF, complexes CoL form CoL(DMF) adducts with the solvent. The base pyridine has to compete for axial coordination according to Equation (3).

$$CoL(DMF) + py \rightleftharpoons CoL(py) + DMF \quad (3)$$

Henry Constant, K_H, for the System O_2/DMF at Various Temperatures

The determination of the temperature dependence of the equilibrium constant K_{O_2} for adduct formation according to Equation (1) requires a knowledge of the Henry constant, K_H, for the temperature range studied. An O_2-sensitive optode was used to determine $[O_2]$, the equilibrium concentration of dioxygen in O_2-saturated DMF at various temperatures (see Experimental Section and Figure S1, Supporting Information). The data obtained for K_H are presented in Table 3.

Table 3. Henry constant, K_H, for the system O_2/*N*,*N*-dimethylformamide in the temperature range 298–223 K.

T [K]	$K_H \times 10^6$ [M Torr^{-1}][a]	T [K]	$K_H \times 10^6$ [M Torr^{-1}][a]
298	6.4	243	7.4
283	6.6	238	7.5
273	6.8	233	7.6
263	7.0	228	7.7
253	7.2		

[a] The error limits for K_H are approximately ±10%.

Equilibrium Constant, K_{O_2}, for Adduct Formation with Dioxygen at Various Temperatures

The Henry constant, K_H, for the system O_2/DMF increases with decreasing temperature (see Table 3) and so does the equilibrium concentration of dioxygen in DMF. As a consequence, adduct formation according to Equation (1) and, correspondingly, the UV/Vis spectra of complexes **1**–**7** in O_2-saturated DMF are shifted towards the dioxygen adducts CoL·O_2. As an example, Figure 2 shows a selection of spectra obtained for the system **1**/O_2/DMF at various temperatures. There are a number of sharp isosbestic points indicating that, in addition to the formation of the 1:1 adduct, there is no further formation of a 1:2 adduct. In line with this, the absorbance data at 406 nm can be well fitted with Equation (8) (see Figure 2, bottom), as derived for monoadduct formation. The fitting procedure finally leads to data for ΔH^o, ΔS^o, and K_{O_2} for complexes **1**–**3** and **5**–**7** (Table 4). The results for complex **4** are missing due to the limited stability of **4** against auto-oxidation.[16]

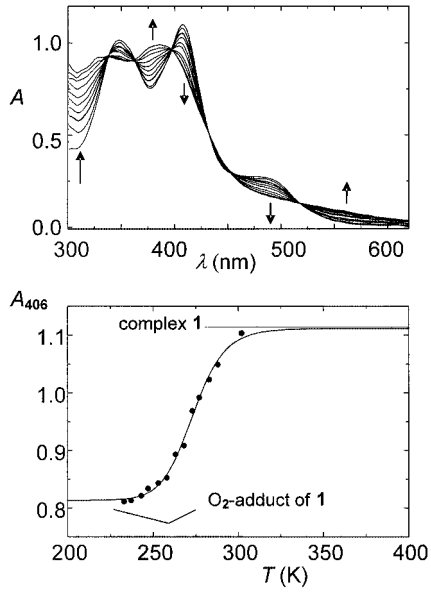


Figure 2. UV/Vis spectra of complex **1** in O_2-saturated *N*,*N*-dimethylformamide at various temperatures (upper diagram; the arrows indicate spectral changes associated with decreasing temperature) and the dependence of the absorbance at 406 nm on the temperature in the range 298–228 K [lower diagram; the fitting curve was obtained by fitting Equation (8) to the (A_{406},T) data].

To have a different experimental method for control, complex **3** in Ar-saturated DMF was titrated with dioxygen at 288 K. The observed spectral changes led to (A_{412},$[O_2]$) data (A_{412} = absorbance at 412 nm) that could be satisfyingly fitted with Equation (9) (see Figure S2, Supporting Information). The equilibrium constant K_{O_2} = 96 ± 9 M^{-1}, as obtained at 15 °C by this titration method (see Table 4), agrees within the limits of error with K_{O_2} = 130 ± 25 M^{-1}, as calculated for 15 °C from the data obtained at various temperatures.

In O_2-saturated DMF, the UV/Vis spectra of complexes **1**–**7** show absorption bands at about 340, 380, and 550 nm (shoulder), even at ambient temperature. These bands can be assigned to M→L charge-transfer processes in the adducts CoL·O_2 and superoxo species $CoL^+ \cdot O_2^-$, respectively (see also EPR data below).[19] In the case of complex **8**, spectral changes associated with the formation of the O_2 adduct were not observed at ambient temperature, but clearly at 223 K.

It follows from Table 4 that complexes **1**–**3** and **5**–**7** do not differ drastically in their dioxygen affinity. At 25 °C, K_{O_2} ranges from 21.9 M^{-1} for **5** to 155 M^{-1} for **7**. The thermo-

Table 4. Summary of thermodynamic data describing the addition of dioxygen to complexes **1**–**7**, according to Equation (1), in *N*,*N*-dimethylformamide and selected data for 1:1 adducts of cobalt(II) complexes with dioxygen.

Complex	Solvent/base	ΔH° [kJ mol^{-1}]	ΔS° [J K^{-1} mol^{-1}]	K_{O_2} [M^{-1}] at 298 K	$10^4 \times K_{O_2}$ [Torr^{-1}][a] at 298 K	Ref.
1	DMF/–	–65 ± 7	–191 ± 20	24 ± 2	1.56	this work
2	DMF/–	–58 ± 6	–164 ± 22	35 ± 5	2.22	this work
3	DMF/–	–49 ± 5	–131 ± 24	65 ± 12	4.17	this work
3	DMF/–			130 ± 25 (at 15 °C)		this work
3	DMF/–			96 ± 9[b] (at 15 °C)		this work
4	DMF/–	_[c]	_[c]	_[c]	_[c]	this work
5	DMF/–	–51 ± 8	–147 ± 23	22 ± 3	1.40	this work
6	DMF/–	–58 ± 10	–163 ± 10	50 ± 13	3.22	this work
7	DMF/–	–30 ± 5	–58 ± 13	155 ± 33	9.92	this work
Co(salen)	DMSO[d]/–	–67	–281		20[e]	[17]
Co(saltmen)[f]	diglyme[g]/4-Mepy[h]	–25	–168		1.58	[4]
Co(salophen)[i]	diglyme/4-Mepy	–43.2	–197		18.2	[4]
Co(α-CH_3-salen)[j]	diglyme/4-Mepy	–56.1	–230		63.1[k]	[4]
Co(salMeDPT)[l]	acetone/–	–59	–285		0.33	[5]
Co(acacen)	toluene/pyridine	–72.5	–305		5.74[m]	[18]

[a] Calculated according to $K_{O_2}(\text{Torr}^{-1}) = K_{O_2}(\text{M}^{-1}) \times K_H$ (K_H = Henry constant). [b] As determined by stepwise titration with O_2. [c] Due to auto-oxidation of complex **4** at $T \geq 293$ K, the spectroscopic data obtained were not safe enough to determine to K_{O_2} reliably. [d] Dimethyl sulfoxide. [e] Extrapolated from 20 °C to 25 °C with $\Delta H^\circ = -16$ kcal mol^{-1}, taken from ref.[17] [f] The ligand saltmen carries a tetra-methylated $C(CH_3)_2$-$C(CH_3)_2$ bridge instead of the CH_2-CH_2 bridge in Co(salen). [g] Bis(2-methoxyethyl)ether. [h] 4-Methylpyridine. [i] The ligand salophen is the salen analogue resulting from the condensation reaction between salicylaldehyde and 1,2-diaminobenzene instead of 1,2-diaminoethane. [j] The ligand α-CH_3-salen is a salen analogue resulting from the condensation reaction between 1,2-diaminoethane and 2-hydroxyacetophenone instead of salicylaldehyde. [k] Extrapolated from 10 °C to 25 °C with $\Delta H^\circ = -13.4$ kcal mol^{-1}, taken from ref.[4] [l] The ligand salMeDPT is a pentadentate salen derivative resulting from the condensation reaction between salicylaldehyde and bis(2-aminoethyl)methylamine instead of 1,2-diaminoethane. [m] Extrapolated from 0 °C to 25 °C with $\Delta H^\circ = -17.3$ kcal mol^{-1}, taken from ref.[18]

dynamic data indicate that the driving force for dioxygen complex formation is the favorable enthalpy of reaction, corresponding to metal–dioxygen bond formation and, as a consequence, a strengthening of the coordinate bonds between the metal and the ligand donor atoms. As characteristically observed for all oxygenation processes,[4] the entropies of oxygenation are seen to be negative, due to the loss of the translational entropy of the O_2 molecule and the increase in ligand rigidity.

The general expectation is that an increase of the electron density on the cobalt, as introduced by substituents on the ligand, should favor the reaction described by Equation (1) and increase K_{O_2}. Since the methyl and *tert*-butyl groups on the salicylaldehyde unit and the methyl groups on the diamine bridge in complexes **1**–**3** and **5**–**7** can have steric as well as electronic effects, there is no simple prediction concerning their effect on the electron density on the cobalt. The equilibrium constant K_{py}, however, which describes adduct formation with pyridine (see Table 2), is a useful experimental measure of both the electron density on the cobalt and its accessibility. K_{py} should therefore correlate inversely with K_{O_2}. For group **A** complexes **1**–**3**, this correlation is indeed observed with $K_{py}(\mathbf{1}) > K_{py}(\mathbf{2}) > K_{py}(\mathbf{3})$ vs. $K_{O_2}(\mathbf{1}) < K_{O_2}(\mathbf{2}) < K_{O_2}(\mathbf{3})$. In the case of group **B** complexes **5**–**7**, the order $K_{O_2}(\mathbf{5}) < K_{O_2}(\mathbf{6}) < K_{O_2}(\mathbf{7})$ is less well reflected by the finding $K_{py}(\mathbf{5}) \approx K_{py}(\mathbf{6}) > K_{py}(\mathbf{7})$. The inverse correlation between K_{py} and K_{O_2} confirms convincingly that the reaction of the cobalt(II) complexes CoL with O_2 according to Equation (1) is not at all a simple nucleophilic addition reaction. Obviously, electron abstraction and formation of the species $Co^{III}L^+$ is the driving force, with the latter following the electron density on the cobalt, as determined by the ligand L.[20] The order in the oxidation potential, $E_{1/2}(\mathbf{1}) > E_{1/2}(\mathbf{2}) > E_{1/2}(\mathbf{3})$ (Table 1), is paralleled by the reverse order in dioxygen affinity, $K_{O_2}(\mathbf{1}) < K_{O_2}(\mathbf{2}) < K_{O_2}(\mathbf{3})$. This means that the more easily the cobalt(II) is oxidized, the stronger is the interaction with O_2. The corresponding data obtained for group **B** complexes **5**–**7**, however, are not in line with this sort of correlation.

For comparison, Table 4 lists data for pressure-based equilibrium constants $K_{O_2}(\text{Torr}^{-1})$, as reported for a number of "symmetric" salen-type cobalt(II) complexes that form 1:1 adducts with dioxygen. Neglecting possible solvent effects, one learns that the range of dioxygen affinities obtained for complexes **1**–**3** and **5**–**7** [$K_{O_2} \approx (0.1–1) \times 10^{-3}$ Torr^{-1}] covers the K_{O_2} data reported for Co(saltmen),[21] Co(acacen), and Co(salMeDPT).[21] The range of affinities reported for Co(salophen),[21] Co(salen), and Co(α-CH_3-salen)[21] is approximately one order of magnitude higher [$K_{O_2} \approx (2–6) \times 10^{-3}$ Torr^{-1}], but, as a rule, increased affinity means reduced resistance against oxidative attack.

To summarize: (i) compared to Co(salen), the "unsymmetric" salen-type ligands of the present study lead to cobalt(II) complexes with slightly reduced dioxygen affinities, and (ii) the loss in dioxygen affinity is paralleled by an increase in resistance towards irreversible auto-oxidation. Depending on the type of substitution (substituents on the CH_2-CH_2 bridge and/or on the phenyl rings), complexes **1**–**3** and **5**–**7** are O_2-active cobalt(II) compounds with interesting intermediate properties concerning sufficient dioxygen affinity (and possible catalytic activity) on the one hand and

limited susceptibility to auto-oxidation on the other hand. As an example, in the case of complex **3** the binding constant for O_2 (in DMF) is five times smaller than in the case of Co(salen) (in DMSO). Compared to Co(salen), complex **3** is, however, far more auto-oxidation resistant (at ambient temperature, air-saturated solutions of **3** in DMF are stable for several days). The affinity constant K_{O_2} = 65 M^{-1} for **3** means that, in an O_2-saturated solution of **3** in DMF at 25 °C, not less than 24% of the complex is present in the form of the O_2 adduct.

EPR Spectra of the Dioxygen Adducts of Complexes 3 and 7 in Frozen DMF

We reported earlier that in frozen O_2-saturated solution the O_2 adducts of cobalt(II) complexes with "symmetrically" substituted salen ligands show EPR spectra with well-resolved hyperfine structures.[22] As confirmed by the investigation of complexes **3** and **7**, the "unsymmetrically" substituted cobalt(II) complexes of the present study behave analogously. As an example, Figure 3 shows the experimental and simulated ESR spectrum of the 1:1 dioxygen adduct of complex **3** in O_2-saturated frozen DMF. The EPR data, as obtained by computer simulation, are summarized in Table 5.

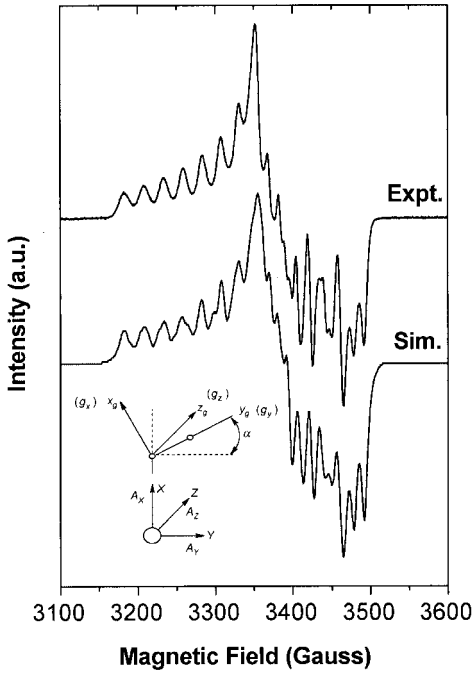


Figure 3. Experimental and simulated X-band ESR spectrum of the dioxygen adduct of complex **3** in O_2-saturated frozen DMF [inset: coordinate system for Zeeman and hyperfine terms of ESR spectra of CoL·O_2 adducts. The principal g axes are x_g, y_g, and z_g, and the principal A axes are X, Y and Z. According to the Smith and Pilbrow notation:[24a] $X(z)$, $Y(y)$ and $Z(x)$, $A_x(Z) = A_Z$, $A_y(Y) = A_Y$, $A_z(X) = A_X$].

As documented earlier, the unpaired electron density in the 1:1 adducts resides mostly on the O_2 moiety.[22] The g-values lie close to the free-electron value and the hyperfine structure arising from the cobalt nucleus (I^{Co} = 7/2) is still present but, compared to CoL Schiff-base complexes in the absence of dioxygen, is strongly reduced in magnitude. The oxygenation of complexes **3** and **7** was found to be complete and the results obtained are in agreement with the general experience that the stability of such 1:1 adducts is enhanced by additional coordination of a base B (in the present system, B = DMF) in the sixth (axial) position *trans* to O_2.

The electronic structure of the O_2 adducts of cobalt(II) complexes is usually discussed in terms of a spin-pairing model, which interprets the cobalt hyperfine structure, observed in the EPR spectra of the adducts, as originating from a direct or indirect (spin-polarization) mechanism.[23] The rather low values of $A_y(Y)$ and $A_x(Z)$ (see Table 5) for the O_2 adducts of complexes **3** and **7** in DMF, which acts as a weak base, and the significant reduction in $A_y(Y)$ and $A_x(Z)$ for the dioxygen adduct of complex **3** in the presence of pyridine, which acts as a strong base, are most probably due to the peculiar balance between the direct and indirect (spin-polarization) contributions to the ^{59}Co hyperfine coupling constants.

In discussing the relationship between g-values and the electronic structure of the O_2 adducts of **3** and **7**, one has to consider the fact (see Table 5) that the g_x and g_z values are close to the free-electron value (2.0023), whereas the data for g_y (along O–O bond) are somewhat greater. This increase in g_y can be rationalized in terms of the energy separation of the dioxygen π*-orbitals.[23,24] According to Equation (4), the size of g_y is controlled by the oxygen spin-orbit coupling parameter, λ, and by the energy separation, Δ, between the π*-dioxygen orbitals. An increase in g_y corresponds to decreasing values of Δ. This points to a lower energy separation of the oxygen π*-orbitals in the O_2 adducts of the CoL(B) complexes, with B being the weak base DMF. The size of Δ could well be related to the strength of the Co–O_2 interaction.[25] An increase in Δ, due to a strong σ-bond interaction between the cobalt d_{z^2} and oxygen π*-orbital leads to an increased strength of the Co–O_2 bond as well. On the other hand, the increased values of g_y observed for the dioxygen adducts of complexes **3** and **7** in DMF (see Table 5) imply lower Δ values. This may in turn suggest a weaker Co–O_2 interaction of these complexes,

Table 5. Evaluated EPR spin-Hamiltonian parameters for the dioxygen adducts of complexes **3** and **7** in O_2-saturated DMF at 77 K.

Complex	g_x[a]	g_y	g_z	$-A_X^{Co}$[a,b]	$-A_Y^{Co}$	$-A_Z^{Co}$	α [°]
3	2.011	2.092	1.985	23	78	36	25
3[c]	2.009	2.079	1.986	26	59	27	26
7	2.009	2.093	1.987	25	86	29	28

[a] The principal axes of the g and A tensors are defined in Figure 3. [b] The hyperfine splitting constants are given in MHz (for conversion to cm^{-1}, divide values by 3×10^4). In the text, the principal components of the A tensor are denoted as follows: $A_x(Z) = A_Z$, $A_y(Y) = A_Y$, $A_z(X) = A_X$. [c] Solvent: DMF containing 5% (v/v) pyridine.

compared to the O_2 adducts of complexes CoL(B) with a strong base such as pyridine.

$$g_y = 2.0023 + 2\left[\frac{\lambda^2}{\lambda^2 + \Delta^2}\right]^{1/2} \quad (4)$$

Complex 8 as O_2-Activating Catalyst

In O_2-saturated DMF, the symmetrically substituted salen complex **8** is remarkably resistant to irreversible auto-oxidation (see above). At ambient temperature, the UV/Vis spectrum of **8** in O_2-stripped DMF solution does not change upon addition of O_2. At –40 °C, however, reversible adduct formation of **8** with dioxygen according to Equation (1) is observed. This means that, compared to complexes **1**–**7**, the dioxygen affinity of **8** is small. Despite this comparatively limited interaction with dioxygen, complex **8** was found to be a weak catalyst for the O_2-oxidation of triphenylphosphane and 2,6-di-*tert*-butylphenol (DTBP). As shown in Table 6, at ambient temperature 35% of DTBP is oxidized to the corresponding quinone within 24 hours. In the case of PPh_3, 84% of this substrate is oxidized under the same conditions. Although the observed catalytic activity of **8** is very limited, it points to interesting catalytic properties to be expected for complexes **1**–**3** and **5**–**7**. From the point of practical application in catalysis, one is interested in O_2-activating cobalt(II) complexes with intermediate properties concerning the interplay between dioxygen affinity (corresponding to superoxo complex formation) and auto-oxidation rate. Complexes **1**–**3** and **5**–**7** can be suggested as promising candidates.

Table 6. Oxidation of triphenylphosphane (PPh_3) and 2,6-di-*tert*-butylphenol (DTBP) in O_2-saturated *N*,*N*-dimethylformamide according to Equation (10) in the presence of complex **8** as catalyst.

Substrate S	[S] [mM]	[**8**] [mM]	*T* [K]	*t*[a] [h]	Product distribution (%) substrate	oxid. substrate
DTBP	5	0.5	293	24	65	35[b]
PPh_3	10	1	295	5	92	8[c]
PPh_3	10	1	295	24	16	84[c]

[a] Reaction time. [b] 2,6-Di-*tert*-butyl-1,4-benzoquinone. [c] Ph_3PO.

Conclusions

Complexes **1**–**7** are unsymmetrically substituted cobalt(II) complexes of the Co(salen)-type. In solution, all of these complexes behave like Co(salen) in that they interact with dioxygen, according to Equation (1), to form monoadducts with O_2. Due to steric crowding of the ligands, the formation of dinuclear species, as observed for "normal" Co(salen), is obviously suppressed. The spectroscopic information obtained (UV/Vis and EPR) is in line with the interpretation that the monoadducts, $CoL{\cdot}O_2$, are cobalt(III) superoxo compounds.

The resistance against auto-oxidation is ligand-dependent. In air-saturated DMF at ambient temperature, complexes **1**–**3** are stable for several days, **5**–**7** change slowly within one day, and **4** undergoes oxidative decomposition within hours.

The dioxygen affinity of the complexes in DMF, as characterized by the equilibrium constant K_{O_2} for adduct formation with dioxygen, ranges from $K_{O_2} = 21.9\ M^{-1}$ for **5** to $K_{O_2} = 155\ M^{-1}$ for **7** at 298 K. The data obtained for K_{O_2} correlate inversely with the Lewis acidity of the cobalt center, as characterized by the equilibrium constant K_{py} for adduct formation with the base pyridine. As an example, the dioxygen affinity of $K_{O_2} = 65$ for complex **3** means that, in O_2-saturated DMF at 25 °C, not less than 24% of **3** is present in the form of the superoxo species. There is experimental evidence to suggest that the remarkably oxidation-resistant complexes **1**, **2** and **3** in particular are useful catalysts for the oxidation of organic substrates with dioxygen in homogeneous solution under mild conditions.

Experimental Section

Chemicals: The commercially available aldehydes, ketones, and amines needed for ligand synthesis and the salt $Co(AcO)_2{\cdot}4H_2O$ (reagent grade) were used without further purification. Reagent grade *N*,*N*-dimethylformamide (DMF), toluene, and acetonitrile used as solvents for spectrophotometric titrations and CV measurements were stored under Ar.

Ligands: The salen-type ligands used for the preparation of complexes **1**,[26] **3**,[10] and **8**[11] were synthesized according to the literature. The ligands for complexes **2** and **4**–**7** were obtained by a two-step procedure, as developed for the preparation of the "unsymmetric" ligand of complex **3**.[10] In the first step, the corresponding ketone (2′-hydroxyacetophenone or 2,4-pentanedione) was treated with the corresponding diamine (1,2-diamino-2-methylpropane or 1,2-diaminoethane) in a 1:1 ratio to form a tridentate mono Schiff base. In the second step, the mono Schiff base was finally turned into the tetradentate salen-type ligand H_2L by reaction with salicylaldehyde or 3-*tert*-butyl-5-methylsalicylaldehyde. More details concerning the application of this two-step procedure to the preparation of the ligands for complexes **2** and **4**–**7** can be found in the literature.[12]

Complexes: Complex **8** was prepared and characterized as described earlier.[11] To avoid oxidation, the preparation of complexes **1**–**7** according to Equation (5) was carried out under Ar.

$$H_2L + Co(AcO)_2 \rightleftharpoons CoL + 2\ AcOH \quad (5)$$

General Procedure: A solution of 2 mmol of $Co(AcO)_2{\cdot}4H_2O$ in 25 mL of ethanol was added dropwise to a warm solution of 2 mmol of the ligand H_2L in 20–30 mL of ethanol whilst stirring. The red solution was refluxed for 30 min. Upon cooling, the red or red-orange cobalt complex precipitated. Recrystallization was carried out from ethanol (yield: 60–95%).

2: $C_{19}H_{20}CoN_2O_2$ (367.31): calcd. C 62.13, H 5.49, N 7.63; found C 61.89, H 5.52, N 7.58.

3: $C_{24}H_{30}CoN_2O_2$ (437.44): calcd. C 65.90, H 6.91, N 6.40; found C 65.82, H 7.09, N 6.44.

4: $C_{14}H_{16}CoN_2O_2$ (303.22): calcd. C 55.46, H 5.32, N 9.24; found C 55.06, H 5.34, N 9.04.

5: $C_{19}H_{26}CoN_2O_2$ (373.36): calcd. C 61.12, H 7.02, N 7.50; found C 61.07, H 7.26, N 7.48.

7: $C_{21}H_{30}CoN_2O_2$ (401.42): calcd. C 62.84, H 7.53, N 6.98; found C 62.87, H 7.62, N 7.00.

The identity of complexes **1** and **6** was based on the purity of the ligands applied (CHN, ^{1}H NMR) and on the spectroscopic properties of the complexes (IR, UV/Vis). The visible absorption data of complexes **1**–**8** are presented in Table S1.

Instrumentation: UV/Vis spectra: diode array spectrophotometer (HP, type 8451A). Cyclic voltammetry: CV setup as described earlier.[11] Determination of dioxygen dissolved in DMF: optode (= dioxygen sensor), based on fluorescence quenching.[27] EPR spectra: Bruker SRC 200 D spectrometer, operating at X-band, with variable-temperature unit. An Ar-filled glove box was used for the preparation of O_2-stripped solutions.

Stability of the Complexes in Solution: The stability of complexes **1**–**8** in solution in air-saturated DMF was followed by monitoring the change of the UV/Vis spectra with time at ambient temperature.

Determination of Equilibrium Constant K_{py}: The stepwise titration of freshly prepared solutions of complexes **1**–**8** in toluene (Ar-saturated) with pyridine (Ar-saturated) according to Equation (2) was followed spectrophotometrically at 298 K in the range λ = 350–600 nm. Least-squares fitting of Equation (6) to the (A,[py]) data led to the equilibrium constant K_{py} (A = absorbance).

$$A = (A_o + A_\infty K_{py}\,[py])/(1 + K_{py}\,[py]) \quad (6)$$

The parameters A_o and A_∞ refer to the absorbance of the complexes CoL and CoL·py, respectively, at the initial concentration of CoL, $[CoL]_o$.

Cyclic Voltammetry: The measurements were carried out in O_2-stripped (Ar) acetonitrile (0.1 M $[Bu_4N]ClO_4$) at 293 K with [complex] = 1 mM. The scan rate was 100 mV s^{-1}.

EPR Spectroscopy: Solutions of **3** and **7** in DMF (1 mM) were filled into cylindrical quartz tubes and then purged with O_2 or Ar at ambient temperature before cooling to 77 K. The reversibility of dioxygen binding was checked by warming up the oxygenated frozen solutions, purging with Ar, and repeating the low-temperature measurement.

Henry Constant, K_H, for the System O_2/DMF at Various Temperatures: An O_2-sensitive optode[27] was used to determine $[O_2]$ in O_2-saturated DMF in the temperature range 298–228 K at atmospheric pressure. Calibration of the optode was achieved by determining its signal at 228 K in O_2-saturated DMF ($[O_2]_{rel}$ = 100%) and O_2-stripped (Ar) DMF ($[O_2]_{rel}$ = 0%), respectively. As shown in Figure 1S, $[O_2]_{rel}$ increases linearly with T^{-1}. On the basis of $[O_2] = 4.8 \times 10^{-3}$ M, as reported for O_2-saturated DMF at 298 K,[28] the data shown in Figure S1 lead to Equation (7).

$$[O_2] = 1.42 \times 10^{-3} + 1.01 \cdot T^{-1}\ (M) \quad (7)$$

This equation gives the equilibrium concentration of dissolved dioxygen, $[O_2]$, for O_2-saturated DMF at any temperature in the range 298–228 K. The Henry constant, K_H, follows from $[O_2]$ according to $K_H = [O_2]/p_{O_2}$ (in the present system, $p_{O_2} = 760 - p_{DMF}$; p_{DMF} = vapor pressure of DMF in Torr units).

Determination of Equilibrium Constant K_{O_2} for Adduct Formation with Dioxygen at Various Temperatures: A reaction vessel containing 70 mL of the freshly prepared solution of the complex CoL in Ar-saturated DMF ([CoL] ≈ 10^{-4} M) was placed into a thermostat/cryostat for temperature control. The experimental setup allowed us to saturate the solution with either O_2 or Ar. Spectra of the solution (λ = 300–650 nm) were recorded with a specially designed quartz cell (1 cm path length), immersed in the solution. The cell was equipped with flexible quartz fiber cables for connection to a diode array spectrophotometer. For each CoL/O_2 system, spectra were recorded stepwise at 8–12 temperatures in the range T = 310–230 K. In the first step, the solution was thermostatted at a given temperature in the range 25–35 °C and equilibrated with O_2 for 5 min. After that, the first spectrum was recorded. In the next step, the temperature was lowered by approximately 10 °C and the procedure of thermostatting and equilibrating with O_2 for 5 min was repeated to take the second spectrum. To guarantee O_2-equilibration, there was a continuous flow of O_2 through the solution during all steps. Least-squares fitting of Equation (8) to the observed (A,T) data[29] led to the parameters $m = -\Delta H^o/R$, $b = \Delta S^o/R$, A_{CoL}, and A_{add}. The equilibrium constant K_{O_2} was calculated according to van't Hoff.

$$A = \{(A_{CoL} + A_{add}\,[O_2]\exp(mT^{-1} + b)\}/\{(1 + [O_2]\exp(mT^{-1} + b)\} \quad (8)$$

where A_{CoL} and A_{add} refer to the absorbance of the complex CoL and of its dioxygen adduct, CoL·O_2, respectively, at the initial concentration of CoL, $[CoL]_o$.

The reversibility of adduct formation according to Equation (1) was confirmed by repeatedly running the cycle Ar-saturation/O_2-saturation at a given temperature and recording the corresponding spectra. For a given complex CoL, these experiments led to identical spectra for the O_2-saturated solution and for the Ar-saturated solution.

Determination of Equilibrium Constant K_{O_2} by Titration with Dioxygen: In an alternative approach, K_{O_2} at 288 K was determined by stepwise titration of a freshly prepared solution of complex **3** in Ar-saturated DMF with O_2. The titration was carried out in a spherical reaction vessel equipped with an inlet and with a glass tube, the end of which was sealed with a quartz cell fitting into the cell holder of the spectrophotometer. In an Ar-operated glove box, the solution of CoL in Ar-saturated DMF was filled into the reaction vessel. After that, the inlet was sealed with a septum through which twenty portions of O_2 were successively added with a gastight syringe. After each addition, the system was equilibrated at 288 K and a spectrum was recorded. Least-squares fitting of Equation (9) to the observed (A,$[O_2]$) data led to the equilibrium constant K_{O_2}. The data for $[O_2]$ were obtained from the partial pressure of O_2, p_{O_2}, and the Henry constant, K_H, according to $[O_2] = K_H \cdot p_{O_2}$.

$$A = (A_{CoL} + A_{add}\,K_{O_2}\,[O_2])/(1 + K_{O_2}\,[O_2]) \quad (9)$$

Analytical Procedure for Monitoring the Catalytic O_2-Oxidation of Substrates: The oxidation of substrates S according to Equation (10), as catalyzed by **8**, was studied with S = triphenylphosphane and 2,6-di-*tert*-butylphenol. The formation of the oxidation products, $(Ph_3)PO$ and 2,6-di-*tert*-butyl-1,4-benzoquinone, was

monitored by ^{31}P NMR and ^{1}H NMR spectroscopy, respectively.[14]

$$S + O_2 \xrightarrow{CoL} S\ (oxid.) \qquad (10)$$

Supporting Information Available (see also footnote on the first page of this article): Table S1, provides visible absorption data of complexes **1**–**8**. Figure S1 presents the calibration curve for the relative concentration of O_2 in DMF at various temperatures, and Figure S2 presents a plot of the (A_{412},[O_2]) data obtained by spectrophotometric monitoring of the titration of complex **3** with O_2 in DMF.

Acknowledgments

Sponsorship of this work by the Deutsche Forschungsgemeinschaft and Verband der Chemischen Industrie e.V. is gratefully acknowledged. The cooperation between Darmstadt and Bratislava was supported within the framework of the program "Scientific and Technological Cooperation", as established between Germany and the Slovak Republic. The EPR laboratory in the Faculty of Chemical and Food Technology, STU Bratislava, is funded by VEGA 1/2450/05.The authors thank Prof. E.-G. Jäger (Universität Jena) for valuable suggestions concerning the manuscript, Dr. M. Rudolph (Universität Jena) for the possibility to do some CV measurements in his laboratory, and Prof. Dr. B. Speiser (Universität Tübingen) for important information concerning the electrochemical data.

[1] T. Tsumakis, *Bull. Chem. Soc. Jpn.* **1938**, *13*, 252.
[2] a) A. E. Martell, D. T. Sawyer, *Oxygen Complexes and Oxygen Activation by Transition Metals*, Plenum Press, New York, **1988**; b) D. H. R. Barton, A. E. Martell, D. T. Sawyer, *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Plenum Press, New York, **1993**; c) L. I. Simándi, in *Advances in Catalytic Activation of Dioxygen by Metal Complexes* (Eds.: L. I. Simándi, T. M. Simándi), Kluwer Academic Publishers **2003**, *26*, 265.
[3] D. Chen, A. E. Martell, *Inorg. Chem.* **1987**, *26*, 1026.
[4] D. Chen, A. E. Martell, Y. Sun, *Inorg. Chem.* **1989**, *28*, 2647.
[5] E. V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D. H. Busch, *Inorg. Chem.* **1997**, *36*, 2746.
[6] L. I. Simándi, T. M. Simándi, Z. May, G. Besenyei, *Coord. Chem. Rev.* **2003**, *245*, 85.
[7] a) E.-G. Jäger, in *Chemistry at the Beginning of the Third Millenium* (Eds.: L. Fabbrizzi, A. Poggi), Springer-Verlag, Berlin Heidelberg New York, **2000**, p 103; b) E.-G. Jäger, J. Knaudt, K. Schuhmann, A. Guba, in *Peroxide Chemistry − Mechanistic and Preparative Aspects of Oxygen Transfer* (Ed.: W. Adam), Wiley-VCH, Weinheim, **2000**, p 249.
[8] a) C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Eur. J. Inorg. Chem.* **2002**, 2194; b) C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Eur. J. Inorg. Chem.* **2003**, 1948.
[9] a) C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Inorg. Chem.* **2003**, *42*, 8214; b) · S. del Piero, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, *Dalton Trans.* **2004**, *9*, 1358.
[10] A. Böttcher, H. Elias, B. Eisenmann, E. Hilms, A. Huber, R. Kniep, C. Röhr, M. Zehnder, M. Neuburger, J. Springborg, *Z. Naturforsch., Teil B* **1994**, *49*, 1089.
[11] A. Böttcher, H. Elias, E.-G. Jäger, H. Langfelderova, M. Mazur, L. Müller, H. Paulus, P. Pelikan, M. Rudolph, M. Valko, *Inorg. Chem.* **1993**, *32*, 4131.
[12] A. Huber, Dr.-Ing. Dissertation, Technische Hochschule Darmstadt, **1997.**
[13] N. N. Greenwood, A. Earnshaw, *Chemie der Elemente*, VCH, Weinheim, **1988**.
[14] L. Müller, Dr.-Ing. Dissertation, Technische Hochschule Darmstadt, **1996**.
[15] a) E. Eichhorn, Dr. rer. nat.-Dissertation, Universität Tübingen, **1995**; b) Private communication by Prof. Dr. Bernd Speiser, Institut für Organische Chemie, Universität Tübingen; c) A. Nishinaga, K. Tajima, B. Speiser, E. Eichhorn, A. Rieker, H. Ohya-Nishiguchi, K. Ishizu, *Chem. Lett.* **1991**, 1403.
[16] The spectral changes observed during the equilibration of complex **4** with O_2 were clearly affected by partial auto-oxidation of the complex, especially at temperatures above 293 K, and did not allow a reliable determination of K_{O_2}. One can estimate, though, that the dioxygen affinity of complex **4** corresponds to an equilibrium constant $K_{O_2} \geq 200\ M^{-1}$ at 298 K.
[17] E.-I. Ochiai, *Inorg. Nucl. Chem.* **1973**, *35*, 1727.
[18] M. J. Carter, D. P. Rilemma, F. Basolo, *J. Am. Chem. Soc.* **1974**, *96*, 393.
[19] a) A. B. P. Lever, H. B. Gray, *Acc. Chem. Res.* **1978**, *11*, 343; b) V. M. Miskowski, *Inorg. Chem.* **1975**, *14*, 2318; c) T. Freedman, G. Yoshida, T. M. Loehr, *J. Chem. Soc., Chem. Commun.* **1974**, 1016; d) Y. Sasaki, J. Fujita, K. Saito, *Bull. Chem. Soc. Jpn.* **1953**, *26*, 72.
[20] For a detailed thermodynamic description of the reaction described by Equation (1) one has to consider the following scheme: $Co^{II}L(DMF) \rightleftharpoons Co^{III}L(DMF)^+ + e^-$ (step 1), $O_2 + e^- \rightleftharpoons O_2^-$ (step 2), $Co^{III}L(DMF)^+ + O_2^- \rightleftharpoons \{Co^{III}L(DMF)^+\}\text{-}\{O_2^-\}$ (step 3). Obviously, the overall reaction, CoL(DMF) + $O_2 \rightleftharpoons$ CoL(DMF)·O_2, is governed by step 1.
[21] The nature of this modified salen ligand is described in Table 4.
[22] M. Valko, R. Klement, P. Pelikán, R. Boca, L. Dlhán, A. Böttcher, H. Elias, L. Müller, *J. Phys. Chem.* **1995**, *99*, 137.
[23] Both mechanisms, i.e. the direct delocalization of the unpaired spin density into the cobalt 3d orbitals (inducing positive spin density on the cobalt orbitals) as well as the indirect spin-polarization of the 3d orbitals (inducing negative spin density on the cobalt orbitals), contribute to the cobalt anisotropic hyperfine structure. Since the two mechanisms put spin of opposite sign in the d orbitals, the contribution to the ^{59}Co hyperfine splitting constant stemming from the direct mechanism may cancel the one from the indirect mechanism or vice versa. For more details see: a) T. D. Smith, J. R. Pilbrow, *Coord. Chem. Rev.* **1981**, *39*, 295; b) T. D. Smith, I. M. Ruzic, S. Tirant, J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.* **1982**, 363.
[24] a) W. Känzig, M. H. Cohen, *Phys Rev. Lett.* **1959**, *3*, 509; b) H. R. Zeller, W. Känzig, *Helv. Phys. Acta* **1967**, *40*, 845.
[25] a) S. Fukuzumi, K. Ohkubo, *Chem. Eur. J.* **2000**, *6*, 4532; b) S. Fukuzumi, H. Ohtsu, K. Ohkubo, S. Itoh, H. Imahori, *Coord. Chem. Rev.* **2002**, *226*, 71.
[26] R. Warmuth, H. Elias, *Inorg. Chem.* **1991**, *30*, 5027.
[27] T. Scheper, F. Plötz, C. Müller, B. Hitzmann, *Trends Biotechnol.* **1994**, *12*, 42.
[28] D. T. Sawyer, G. Chiericato, C. T. Angelis, E. J. Nanni, T. Tsuchiya, *Anal. Chem.* **1982**, *54*, 1720.
[29] The data for the absorbance *A* were corrected for the temperature dependence of the density of the solvent DMF.

Received: October 21, 2005

