Activation of Molecular Oxygen by Biomimetic Schiff Base Complexes of Manganese, Iron, and Cobalt

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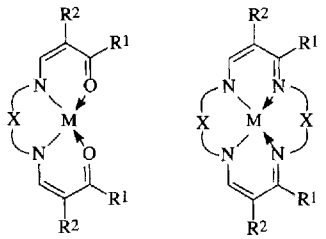
The metal complexes (*E,E*)-[{diethyl 2,2′-[1,2-phenylenebis(iminomethylidyne)]bis[3-oxobutanoato]}(2−)-*N,N′,O³,O³′*]-manganese (Mn**1a**), [3,3′]-[1,2-phenylenebis(iminomethylidyne)bis(2,4-pentanedionato)(2−)-*N,N′,O²,O²′*]manganese (Mn**1b**), and (Z,Z)-[diethyl 3,3′-(1,2-phenylenediimino)bis(2-cyano-2-propenoato)](2−)-*N³,N³′,O¹,O¹′*]manganese (Mn**1c**) were synthesised and the oxygenation of these complexes was investigated by gas volumetry. All complexes except Mn**1c** are able to take up oxygen but with different magnitudes. The catalytic activity of the Mn, Co, and Fe complexes of the ligands **1a** and **1c** and (*E,E*)-[{diethyl 2,2′-[1,2-ethylenebis(iminomethylidyne)]bis[3-oxobutanoato]}(2−)-*N,N′,O³,O³′*] iron (Fe**1d**) and [diethyl (*all-E*)-5,14-dihydro-6,17-dimethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine-7,16-dicarboxylato)(2−)-*N⁵,N⁹,N¹⁴,N¹⁸*]iron (Fe**2a**) has been compared with respect to the oxidation of hydroquinone by molecular oxygen. The results are interpreted with the aid of electrochemical properties, Lewis acidities, and other relevant factors. However, no simple relationship between the catalytic activity and the other factors could be found.

The binding, the transport, and the activation of dioxygen play an important role in biological systems. Since Tsumaki[1] showed in 1938 that the cobalt salicylaldimine complexes prepared by Pfeiffer[2] are able to bind dioxygen reversibly, many suitable model compounds have been developed which can mimic the properties of the biological systems[3] and are able to bind or activate dioxygen.

On the other hand, there exists a wide range of organic compounds which react as substrates by taking up activated oxygen or its oxidation equivalents. One of these compounds is the hydroquinone/quinone pair which plays an important part in biochemical redox processes[4], for instance in the form of the coenzyme Q (ubiquinone) that transfers electrons from NADH to the Fe heme group of cytochrome b in the respiratory chain. The hydroquinone/quinone system is also a suitable and easily regenerable redox system in organic syntheses where the quinone reacts as a hydrogen acceptor becoming a hydroquinone[5].

The 3d metal chelate complexes described here have a certain similarity to salen complexes as well as to the active sites of various redox enzymes. Their advantage is that the peripheral substituents R and the bridge X can be varied in a different manner and can be used for adjusting some of the factors which influence the catalytic activity, e.g. the redox behaviour of the central atom and its acceptor ability against additional axial ligands, the extension of the π-electron system, the symmetry of the complex centre and the spin ground state. Thus, the complexes of the types **1** and **2** should be suitable for the investigation of the relationship between electronical as well as structural features and the catalytic activity of the metal centre. Due to their biological relevance, the elements manganese, iron, and cobalt[6] as central metals in such complexes are of special interest for studies on biomimetic oxygen activation[3h,i,k].

In this article the catalytic activity of a series of complexes of the types **1** and **2** – including some new manganese complexes – was investigated with respect to the activation of molecular oxygen by using the oxidation of hydroquinone as a model reaction.



1 **2**

	X	R^1	R^2
a	phenylene	CH_3	COOEt
b	phenylene	CH_3	$COCH_3$
c	phenylene	OEt	CN
d	ethylene	CH_3	COOEt

Results

Preparation of the Complexes

The syntheses of the cobalt and iron compounds were carried out according to standard methods described earlier by using the metal acetate and the free ligand as starting materials.

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$$H_2L + M^{2+} \leftrightharpoons ML + 2\,H^+ \quad (1)$$

In comparison with Ni^{II}, Co^{II}, and Fe^{II}, the Mn^{II} ion is a harder acid and forms weaker complexes with the relatively soft anions of the ligands. Therefore it is necessary to promote the deprotonation of the chelate ligands with an excess of an auxiliary base.

For the manganese complexes the magnetic moment (5.89–6.03 BM) confirms the high spin state of the central atom. Also for the cobalt complex Co**1c** the magnetic moment of 4.53 BM indicates a high spin state whereas Co**1a** is known to be a low spin complex (2.77 BM). This transition to the high spin state in Co**1c** is caused by the strong electron withdrawing effect of the CN and OEt substituents[7a].

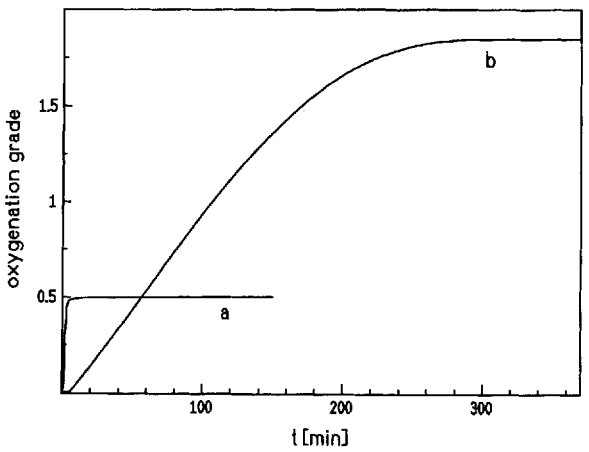
Oxygenation of Manganese Complexes

The measurements were carried out in toluene as a non-coordinating solvent and in pyridine which coordinates rather strongly to one or both axial coordination sites of the complexes.

To quantify the resorption of dioxygen, the ratio $\alpha = n_{O_2}/n_{complex}$ (n: amount in mol) was defined as the degree of oxygenation.

In the case of Mn**1c** · 3 Py (similar to Co**1c** · 3 Py and Fe**1c** · 3 Py in pyridine) neither in toluene nor in pyridine any uptake of dioxygen was observed. The complex Mn**1a** in form of its pyridine diadduct took up dioxygen in toluene very quickly and led (with a half-life of $t_{1/2} < 3$ min) to a constant limiting value $\alpha = 0.5$ (Figure 1, graph a). With an excess of pyridine however, the uptake of dioxygen became more complicated. In pure pyridine the oxygenation of Mn**1a** proceeded more slowly and led to an unexpectedly high but reproducible degree of oxygenation with a stable limiting value of nearly 2 (Figure 1, graph b). The properties of the oxygenation of Mn**1b** are very similar, but in this case the dissolution of the starting material is the rate determining step of the oxygenation. (Mn**1b** is very poorly soluble in toluene but very well in form of its oxygenation product.) Therefore further investigations were carried out with Mn**1a** · 2 Py only.

Figure 1. Oxygenation of Mn**1a** in toluene (a) and in pyridine (b)



Catalytic Measurements

The measurements of the catalytic activity were carried out in acetonitrile as a weakly and in pyridine as a strongly coordinating solvent. Furthermore the use of pyridine guarantees a comparison with the investigations of the oxygenation experiments described above. (Toluene was not suitable for this investigation due to the poor solubility of hydroquinone in this solvent.)

The complexes of manganese, iron, and cobalt with the ligands **1a** and **1c** were investigated to compare the effect of the different central atoms. Furthermore one ethylene-bridged (Fe**1d**) and one macrocyclic (Fe**2a**) complex were included to seize a wide range of ligand structures. For comparison the iron(III) tetraphenylporphyrine complex (Fe^{III}TPP Cl) was used. It has a noticeable but distinctively weaker catalytic activity than those of some of the other compounds.

In order to exclude a non-catalytic oxidation of hydroquinone or a catalysis effected only by the metal ions different kinds of blank tests were carried out. In the pure solvents no oxidation of hydroquinone took place over many hours. Also the solutions of the metal chlorides or other simple metal salts [including simple complexes as the acetylacetonates of Mn^{II}, Fe^{II}, and Co^{II}] did not show any catalytic activity.

In all cases p-quinone is formed according to eq. (2):

$$2\,H_2qu + O_2 \rightarrow 2\,qu + 2\,H_2O \quad (2)$$

In our experiments the sum of the amounts of hydro- and p-quinone was constant and related to the amount of the starting hydroquinone. Therefore, side reactions[8] can be excluded.

For quantification, the turnover numbers (TON) were determined according to the equations (3) and (4).

$$\text{TON(total)} = \frac{n_{qu}}{n_{complex}} \quad (3)$$

$$\text{TON/time} = \frac{n_{qu} - n'_{qu}}{n_{complex} \cdot \Delta t} \quad (4)$$

where: n'_{qu} = amount of p-quinone at the time t [mol]
n_{qu} = amount of p-quinone at the time $t + \Delta t$ [mol]
$n_{complex}$ = amount of complex [mol]
t = time in hours.

The results of the measurement of the catalytic activity are compiled in Table 1.

Redox Behaviour

Table 2 compiles the redox behaviour of the examined complexes. All values of the half-wave potentials were measured against a Ag/AgCl electrode at room temperature.

Only a few compounds, e.g. Fe**1a**, Fe**1d**, Fe**2a**, and Co**1a** in pyridine, show a nearly reversible redox behaviour. For some of the complexes (Fe**1d**, Fe**2a** in acetonitrile) the cyclic voltammograms are not well understood because of their complexity. Presumably, various species (with different coordination numbers or spin states) in both oxidation steps are present. For the complex Co**1c** in pyridine it is assumed that the Co^{II} complex forms a monoadduct which

Table 1. Catalytic activity of the complexes expressed in turnover numbers (TON) per hour (in brackets: TON total)

	Acetonitrile				Pyridine			
	1h	2h	4h	6h	1h	2h	4h	6h
Mn**1a** · 2 Py	200	-	-	-	20	15	15	15
	(200)	(200)	(200)	(200)	(20)	(35)	(65)	(95)
Mn**1c** · 3 Py	7	2	2	2	-	-	-	-
	(7)	(9)	(13)	(17)				
Co**1a**	40	30	20	15	10	-	-	-
	(40)	(70)	(110)	(140)	(10)	(10)	(10)	(10)
Co**1c**	-	-	-	-	-	-	-	-
Fe**1a**	7	3	2	2	2	-	-	-
	(7)	(10)	(14)	(18)	(2)	(2)	(2)	(2)
Fe**1c** · 3 Py	7	2	-	-	-	-	-	-
	(7)	(9)	(9)	(9)				
Fe**1d**	20	-	-	-	190[a]	140	100	50
	(20)	(20)	(20)	(20)	(190)	(330)	(530)	(630)
Fe**2a**	1600[b]	1100	600	200	30	10	-	-
	(1600)	(2700)	(3900)	(4300)	(30)	(40)	(40)	(40)
Fe^{III}TPP Cl	25	-	-	-	50	-	-	-
	(25)	(25)	(25)	(25)	(50)	(50)	(50)	(50)

[a] $n_{(hydroquinone)} = 5.5 \cdot 10^{-4}$ mol ($n_{hydroquinone}/n_{complex} = 1100$). – [b] $n_{(hydroquinone)} = 2.9 \cdot 10^{-3}$ mol ($n_{hydroquinone}/n_{complex} = 5700$).

reacts very quickly after oxidation to afford the diadduct. Therefore no reduction peak of the monoadduct could be obtained. A similar behaviour was observed in the case of Mn**1a**. In these cases no half-wave potentials could be determined.

Table 2. Half-wave potentials of the investigated compounds[a] regarding the redox couple M^{II}/M^{III}

	Acetonitrile [mV]			Pyridine [mV]		
	$E_{1/2}$	E_{pa}	E_{pc}	$E_{1/2}$	E_{pa}	E_{pc}
Mn**1a**	+427	+567	+277	[b]	+772	+97
Mn**1c**	[c]				+990	[d]
					+1260	[d]
Co**1a**[12a]	(+507)	+657	+357[e]	-28	+22	-78
Co**1c**	[c]			[b]	+767	+191
Fe**1a**	[c]			+422[7d]	+452	-392
Fe**1c**	[c]			(+652)[7d]	+682	+562[e]
Fe**1d**		ca. +700	[d]	+300	+253	+347
Fe**2a**	+697[12b][f]	+733	+655	+102	+154	+49
	-967[12b]	+1000	+924			

$E_{1/2}$: half-wave potential; E_{pa}: anodic peak; E_{pc}: cathodic peak. – [a] vs. Ag/AgCl/0.25 M nBu$_4$NCl in acetonitrile; the potential of this reference electrode was calibrated with numerous Cu and Ni complexes of the types **1** and **2** which were independent of the solvent with respect to SCE (+240 mV) and SAE (+196 mV); The potentials were transformed into NHE values [$E_{obs.}$ – 163(9) mV = E_{NHE}]. – [b] Not determinable. – [c] Not determined. – [d] Re-oxidation peak not determinable. – [e] Re-oxidation peak flattened. – [f] First oxidation peak.

Discussion

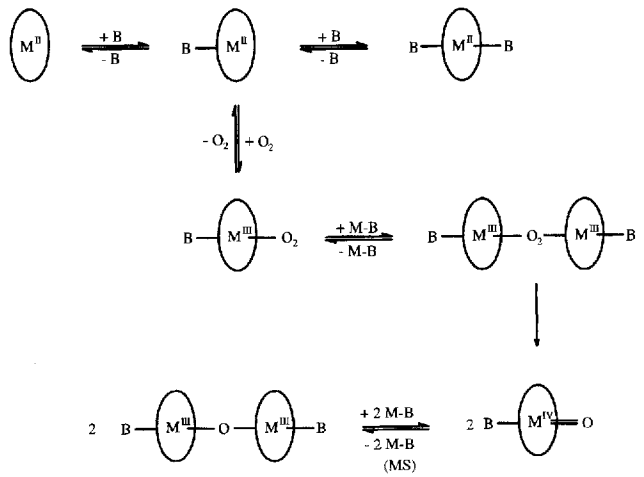
Oxygenation of Manganese in Comparison with Cobalt and Iron Complexes

Scheme 1 shows the possible types of oxygen adducts which could arise from the treatment of the complexes with dioxygen. It considers the essential equilibria only but not the ways of their adjustment. Due to the complexity of the equilibria one can assume that for the explanation of the reaction with dioxygen and the types of the formed oxygenation products various different aspects have to be considered, e.g. the effects of the equatorial ligand and the trans effect of the axial base on the redox potentials and the Lewis acidity of the central atom[10a].

The trans influence of one axial N base (Scheme 1, line 1) favours the oxygenation due to the increasing electron density at the central metal. (An oxygenation without an axial base was observed only in the case of our cobalt Schiff base complexes in a xenon matrix[10b]). The equatorial ligands influence the Lewis acidity and the "softness" of the vacant coordination site at the central atom in a different manner. Consequently, they affect the affinity of the complexes to bind either the partially reduced dioxygen (O_2^-, O_2^{2-}) or an additional N donor base.

The addition of a second N donor molecule (Scheme 1, line 1) blocks the sixth coordination site. Thus the oxygenation is inhibited when the metal atom favours to bind a N base instead of dioxygen. These facts explain why the complexes Mn**1c** and Co**1c**[10c] being the strongest Lewis acids are inactive even at relatively low base concentrations.

Scheme 1. Mechanism of oxygenation



For Mn**1a** · 2 Py the ratio of complex to dioxygen is 2:1. According to Scheme 1, there are two possibilities of realising this degree of oxygenation. One is the formation of a μ-peroxo compound with manganese(III), the other one is an oxo species with manganese(IV). There are examples of both possibilities in the literature describing such adducts with manganese porphyrines and salenes[11,12].

Until now no explanation has been found for the high degrees of oxygenation ($\alpha \approx 2$) of Mn**1a** and Mn**1b** in pyridine. Such a value has not been found for complexes of other central atoms with the same ligands. Since in other cases of oxygen binding and activation with such complexes (Fe**1a** and Co**1a**) no oxidation or oxygenation of the ligands have been observed, the corresponding manganese compounds are expected to become oxygenated at the metal centre rather than at the ligand. A possibility could be the formation of a bisperoxo species [$MnL(O_2)_2$] with manganese in the oxidation state +VI, which is to our knowledge

not described so far. ESR spectroscopic measurements show residues of manganese(II) and a peak at a *g*-value of 2.00(0.05), a range which is typical for organic radicals. Due to the very small peak width of 2 Gauss however, organic radicals can be excluded. This peak has not yet been assigned unambiguously. Both, the formation of a superoxo radical or a manganese ion in an oxidation state of +VI could be possible. Unfortunately in all cases attempts to obtain crystals have failed so far.

The oxygenation of some of the Co and Fe complexes of the types **1** and **2** is described in ref.[7b-d,10a-c,10h-l].

In contrast to the oxygenation of the manganese compound, the complexes Co**1a**[10k] and Fe**1a**[10l] exhibit a stable limiting value of exact $\alpha = 0.50$ also in pure pyridine. The complex Co**1a** shows characteristic absorption bands at 568 nm and 770 nm[10a] which can be assigned to a μ-peroxo species[10c,i]. In the case of Fe**1a** it was not possible to identify unambiguously the oxygenated species in solution. Both, a μ-peroxo Fe^{III} or an oxo Fe^{IV} species could be discussed. Unfortunately the isolation of the corresponding solid has failed so far.

Some of the macrocyclic complexes of Co and Fe (e.g. Co**2a**[10c,k] and the derivative of Fe**2a** in which the bridges X = C_2H_4[10b,e]) showed oxygenations with $\alpha > 1$. However, in contrast to the manganese complexes described above they do not lead to a definite limiting value since the degree of oxygenation increases permanently. This is probably caused by a slow ligand oxidation and/or oxygenation similar as it is observed with Co(acacen) at room temperature[10m].

On the other hand, the use of the iron complex Fe**1d** resulted in a definite oxygen uptake with $\alpha = 0.25$, indicating the formation of a μ-oxo derivative[10f] (Scheme 1, line 3) which is the usual case with iron chelate complexes containing porphyrine or Schiff base ligands. In the case of our compounds only a few are able to form such μ-oxo species (e.g. Fe**1d** and Fe**2a**). Their existence could not only be proven by the degree of oxygenation ($\alpha = 0.25$), but also by the magnetic susceptibility (antiferromagnetic interactions) and the molecular peak in the MS. It is interesting to note that one of the main fragments of the MS of Fe**1d** is the oxo species Fe^{IV}=O formed by splitting of the μ-oxo complex as shown in line three of Scheme 1[13].

A Comparing Discussion of Catalysis

The highest catalytic activity exhibits the complex Fe**2a** in acetonitrile. All the other investigated compounds are at least one order of magnitude less active and most of them show a significantly lower lifetime.

In dependence on the solvent the complexes show great differences in the catalytic activity. When pyridine is used as solvent the activity and the lifetime of Fe**1d** increases dramatically compared to catalysis in acetonitrile. All the other compounds (with the exception of Mn**1a**) exhibit only a slight activity in pyridine and also a lower lifetime than in acetonitrile.

For a discussion of these results some important properties of the complexes should be considered:

Characteristic for all investigated complexes is the fact that catalysis could only be observed with such compounds which are able to take up dioxygen.

The primary step in the catalytic cycle is assumed to be a simple addition of dioxygen to the monoadduct of the complex (eq. 8) independent of secondary reactions. This reaction can be divided formally in the redox reactions (eq. 5 and 6) and a Lewis acid-base interaction (eq. 7). The reactions (5) and (7) are influenced by the change of the electron density at the central atom in an opposite way. Therefore it is difficult to predict the optimal conditions for the activation of dioxygen.

$$B\text{-}ML \rightarrow B\text{-}ML^+ + e^- \quad (5)$$

$$O_2 + e^- \rightarrow O_2^- \quad (6)$$

$$B\text{-}ML^+ + O_2^- \rightarrow B\text{-}ML\text{-}O_2 \quad (7)$$

$$B\text{-}ML + O_2 \rightarrow B\text{-}ML\text{-}O_2 \quad (8)$$

A comparison of the catalytic activity of the complexes with their redox potentials show that there is no direct relationship between these two properties.

For the redox potentials two aspects could be concluded: the addition of an axial base increases the electron density at the metal centre and promotes the oxidation, i.e. the redox potentials decrease. On the other hand, a decrease of electron density, e.g. caused by electron-withdrawing ligands increases the value of the redox potential. Thus the values of the half-wave potentials differ very strongly, depending on the central atom, the ligand and the solvent. Even the two complexes which show the highest catalytic activity (Fe**1d** in pyridine and Fe**2a** in acetonitrile) have strongly different redox potentials. On the other hand, the potentials of Mn**1a** in acetonitrile and Fe**1a** in pyridine are comparable but there is a large difference in the catalytic activity of these two complexes.

The other main factor which influences the behaviour of the complexes regarding the oxygenation as well as the catalytic activity is their Lewis acidity. Direct measurements of the Lewis acidity on iron, cobalt, and manganese complexes are difficult due to their non-planar structure in solution. For a relative comparison of the effect of different equatorial ligands we used data which were measured on planar nickel complexes using pyridine as model base[14a,b]. A similar order was found in the case of the addition of pyridine to organocobalt(III) derivatives[14c] where the organic group is bound axially to the central atom. Although these results cannot be simply transferred to other metal complexes, some influences like inductive effects of the peripheral substituents should be independent of the central atom. Table 3 compiles the equilibrium constants of the reaction (9) and (10) for several nickel and ethylcobalt complexes, respectively.

$$NiL + 2\,B \rightleftharpoons NiL \cdot B_2 \quad (9)$$

$$EtCoL + B \rightleftharpoons EtCoL \cdot B \quad (10)$$

From these complexes the M**1d** and M**2a** compounds show the lowest equilibrium constants whereas M**1a** and

Ni**1c** have medium to high stability constants, i.e. they are relatively strong Lewis acids.

Table 3. Equilibrium constants of nickel and ethylcobalt chelate complexes

	Ni^{II}		Et-Co^{III}	
	β_2 [$l^2 \cdot mol^{-2}$]	log β	β [l·mol]	log β
1a	0.033	−1.48	620.0	2.79
1c	$7.4 \cdot 10^4$	4.87	-[a]	-
1d	$\sim 4 \cdot 10^{-4}$	~−3.4	270.0	2.43
2a	$< 10^{-4}$	≤ −4	6.0	0.78

[a] Not determined.

In the case of the ligand **1c** the strongly electron-withdrawing effect of the peripheral substituents increases the Lewis acidity to such a degree that the σ donor solvent molecules cannot be displaced by dioxygen. This is true for all the central atoms included in this investigation. The same fact is possibly responsible for the lower activity of M**1a** complexes in pyridine as the stronger σ donor compared with acetonitrile. In the case of Fe**1d** and Fe**2a** the Lewis acidity in the Fe^{II} state is low enough (but the affinity of the sixth coordination site to bind the superoxide radical ion in the iron(III) state is high enough) for a replacement of solvent molecules by dioxygen which leads to catalytic activity.

Possible Mechanisms of Activity and Inhibition

The formation of oxo adducts according to Scheme 1 seems to be an important factor for the catalytic activity of the complexes. The highest catalytic activity was observed for those compounds which are able to form μ-oxo derivatives, i.e. Fe**1d** and Fe**2a**. This might result from an optimal steric orientation of the ligand structure which allows the synchronic transfer of electrons and protons. It is possible that the carbonyl substituents of the ligands play a role as a part of "molecular wires" in this transfer. Another possible active species is an oxo-Fe^{IV} derivative which might occur in very low concentrations during the catalytic cycle. Complexes wich form mainly μ-peroxo and superoxo compounds are less active catalysts and react more slowly.

Since the activated dioxygen can be able to decompose the ligands, the stability of the complexes plays an important role regarding the lifetime of the catalysts. The stability depends strongly on the solvent. This can be seen clearly in the case of the macrocyclic complex Fe**2a** which is very stable in acetonitrile (high activity over a long period) but it appears to decompose quickly in pyridine (so after 2 hours no turnover can be observed), whereas in the case of the ethylene bridged compound Fe**1d** the opposite effect seems to be true.

Another possibility for the inhibition of catalyses is the addition of *p*-quinone as a vinylogue of dioxygen to the metal centre[15]. Adducts of *p*-quinone with different Schiff base complexes of Co and Fe have been isolated and characterised as stable solids[15a]. This way of quenching is supposed in the case of the Mn**1a** compound. Samples which contain equimolar amounts of hydroquinone and *p*-quinone display much less activity (TON = $30 \cdot h^{-1}$) than those without an addition of *p*-quinone (TON = $200 \cdot h^{-1}$).

From these considerations follows that the catalytic activity of the complexes is determined by a very complicated set of different parameters and influences. Further investigations are necessary to reveal those factors and to optimise the catalytic activity.

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Experimental

The synthesis of the complexes were carried out under argon. All solvents were dried and distilled before use by standard methods. Cobalt(II) acetate tetrahydrate was purchased from Aldrich and used without further purification. The syntheses of the ligands[16] and the iron(II) complexes[10d,16d,17] were carried out as reported in the literature. $MnBr_2(THF)_2$ was prepared according to a literature method[18]. Hydroquinone was used as purchased by Merck.

Elemental analyses were performed with a Leco CHNS 932 analyser. The metal content was determined by standard methods[19]. – Mass spectra: FINNGRAN MAT SSQ 710. – ESR spectra: ERS 300 ZWG (Berlin). – Magnetic moments were determined with a Gouy balance at four different magnetic fields. – Cyclic voltammetry was performed in a three-electrode cell under a blanket of solvent-saturated argon by using a home-built computer-controlled instrument. Potentials are referred to a Ag/AgCl electrode in acetonitrile containing 0.25 M tetra-*n*-butylammonium chloride. The uptake of dioxygen was measured by using a gas volumetric apparatus constructed by Rudolph[7b]. – The catalytic activity of the complexes was investigated by means of a Chrompack 9001 equipped with a FID detector by using a fused silica capillary column CP-Sil-5 CB, 25-m × 0.22-mm i.d. (H_2 as carrier gas), with internal standard methods.

Preparation of the Mn^{II} Complexes. – General Procedure: The ligand and $MnBr_2(THF)_2$ were dissolved in 20 ml of methanol. The solution was refluxed while 0.03 mol of $NaOCH_3$ was added dropwise until a lemon yellow product precipitated. The suspension was heated for 10 min, then the solid was collected and dried in vacuo. For purification the product was extracted with 10 ml of pyridine.

Bispyridine Adduct of (E,E)-[[{Diethyl 2,2'-[1,2-phenylenebis(iminomethylidyne)]bis(3-oxobutanoato)}(2−)-N,N',O³,O³']-manganese (Mn**1a** · 2 Py): According to the general procedure Mn**1a** was obtained by reaction of 7.79 g (0.02 mol) of ligand **1a** with 7.18 g (0.02 mol) of $MnBr_2(THF)_2$. Yield: 9.47 g (79%). – μ_{eff} = 5.89 BM. – MS (70 eV); *m/z* (%): 441 (100) [Mn**1a**$^+$], 396 (8.3) [Mn**1a**$^+$ − C_2H_5O]. – $C_{30}H_{32}MnN_4O_6$ (599.5): calcd. C 61.80, H 5.04, Mn 9.08, N 9.28; found C 61.23, H 5.38, Mn 9.16, N 9.35.

Mono Pyridine Adduct of [3,3']-[1,2-Phenylenebis(iminomethylidyne)bis(2,4-pentanedionato)(2−)-N,N',O²,O²']-manganese (Mn **1b** · Py): According to the same procedure, Mn**1b** · Py was obtained by adding 7.18 g (0.02 mol) of $MnBr_2(THF)_2$ to 6.57 g (0.02 mol) of the ligand **1b**. Yield: 7.27 g (79%). – μ_{eff} = 5.99 BM. – MS (70 eV); *m/z* (%): 381 (10) [Mn**1b**$^+$], 43 (96.7) [CH_3CO^+]. – $C_{23}H_{23}MnN_3O_4$ (460.4): calcd. C 60.00, H 5.04, Mn 11.93, N 9.13; found C 59.52, H 4.99, Mn 11.81, N 9.07.

Trispyridine Adduct of (Z,Z)-[{Diethyl 3,3'-(1,2-phenylenediimino)bis(2-cyano-2-propenoato)}(2−)-N3,N3',O¹,O¹']-manganese (Mn**1c** · 3 Py): For the preparation of Mn**1c** · 3 Py 7.09

g (0.02 mol) of the ligand **1c** was allowed to react with 7.18 g (0.02 mol) of $MnBr_2(THF)_2$. Yield: 10.44 g (81%). – μ_{eff} = 5.89 BM. – Under common conditions (MS, 70 eV) no molecular peak was obtained, only the peak of the ligand could be observed. Under the condition of chemical ionisation with xenon as auxiliary gas the negatively charged ion of the complex could be observed: *m/z* (%): 407 (41.7) [Mn**1c**$^-$]. – $C_{33}H_{31}MnN_7O_4$ (644.6): calcd. C 61.49, H 4.84, Mn 8.52, N 15.19; found C 62.07, H 4.58, Mn 8.43, N 15.05.

Bismethanol Adduct of (E,E)-[{Diethyl 2,2'-[1,2-phenylenebis(iminomethylidyne)]bis(3-oxobutanoato)}(2–)-N,N',O^3,O$^{3'}$]-manganese (**Mn1a** · 2 CH_3OH): The compound with two axial methanol ligands was prepared by the same procedure from 7.79 g (0.02 mol) of **1a** and 7.18 g (0.02 mol) of $MnBr_2(THF)_2$ except that the precipitate obtained from methanolic solution was recrystallised from methanol (not in pyridine). Yield: 8.29 g (82%). – μ_{eff} = 6.03 BM. – MS (70 eV); *m/z* (%): 441 (100) [Mn**1a**$^+$], 396 (8.3) [Mn**1a**$^+$ – C_2H_5O]. – $C_{22}H_{30}MnN_2O_8$ (505.4): calcd. C 61.49, H 4.85, Mn 10.87, N 5.54; found C 62.10, H 4.78, Mn 10.82, N 5.58.

Preparation of (E,E)-[{Diethyl 2,2'-[1,2-phenylenebis(iminomethylidyne)]bis(3-oxobutanoato)}(2–)-N,N',O^3,O$^{3'}$]cobalt[7a,15] (Co**1a**): 15 g (0.03 mol) of the ligand **1a** was dissolved in 250 ml of ethanol. To the obtained solution a solution of 9.6 g (0.03 mol) of cobalt(II)acetate tetrahydrate in 75 ml methanol was added dropwise whereas the colour of the solution turned red. A red precipitate formed upon cooling which was washed with methanol and dried in vacuo. For purification the product was recrystallised from dioxane. Yield: 11.1 g (64.5%). – m.p. 215°C. – μ_{eff} = 2.77 BM. – MS (70 eV); *m/z* (%): 445 (100) [Co**1a**$^+$], 400 (30.9) [Co**1a**$^+$ – C_2H_5O]. – $C_{20}H_{22}CoN_2O_6$ (445.3): calcd. C 53.92, H 4.98, Co 13.24, N 6.29; found C 53.43, H 5.04, Co 13.30, N 6.32.

Preparation of (Z,Z)-[{Diethyl 3,3'-(1,2-phenylenediimino)-bis(2-cyano-2-propenoato)}(2–)-N3,N3',O^1,O$^{1'}$]cobalt[7a,20] (Co**1c**): 7.5 g (0.02 mol) of the ligand **1c** was dissolved in a mixture of 120 ml of ethanol and 100 ml of dioxane. To the boiling solution a solution of 5.3 g (0.02 mol) cobalt(II)acetate tetrahydrate in 40 ml of methanol was added dropwise. The mixture was allowed to cool yielding an orange complex. Yield: 6.5 g (74.4%). – μ_{eff} = 4.53 BM. – MS (70 eV); *m/z* (%): 411 (4.7) [Co**1c**$^+$]. – $C_{18}H_{16}CoN_4O_4$ (411.3): calcd. C 52.49, H 6.26, Co 14.00, N 12.99; found C 52.57, H 6.17, Co 14.12, N 13.10.

Oxygenation of Manganese Complexes: The investigations were carried out with 0.011–0.034 M solutions under pure oxygen at room temp. When the volume of dioxygen in the apparatus was constant over a period of 30 minutes the measurement was started by the addition of the complex. The value of the volume of oxygen in the apparatus was registered continuously versus time by a plotter.

Catalytic Oxidation of Hydroquinone: A typical sample includes $2 \cdot 10^{-4}$ mol ($4 \cdot 10^{-2}$ M) of hydroquinone, $5 \cdot 10^{-7}$ mol ($1 \cdot 10^{-4}$ M) of the catalyst and the internal standard dissolved in 5 ml of acetonitrile or pyridine. Toluene (0.01 M) and *cis*-decaline (0.02 M) were used as internal standards in acetonitrile and pyridine, respectively. The measurements were carried out at room temp. The oxidation was effected by pure dioxygen under atmospheric pressure. The catalyses were started by the addition of the metal complex. The formation of *p*-quinone and the decrease of the hydroquinone concentration were tested by GC. A reproduction experiment was carried out with Co**1a**. It led to an error of ±3 TON/h. At higher turnover numbers (TON ≥ 100) the error was about ±5%.

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[8] In some cases the amount of *p*-quinone does not correspond with the consumed amount of hydroquinone (e.g. certain cobalt complexes without pheripheral carbonyl groups at the ligand). This fact can be explained by a two-electron reduction of dioxygen according to eq. (2a) yielding hydrogen peroxide which reacts with consumption of p-quinone and further consumption of dioxygen to different secondary reactions.

$$H_2qu + O_2 \rightarrow qu + H_2O_2 \qquad (2a)$$

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