Catalytic oxidation of thiols on polymer attached cobalt phthalocyanine complexes

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J. ZWART

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PROEFSCHRIFT

ter verkrijging van de graad van doctor in de technische wetenschappen aan de Technische Hogeschool Eindhoven, op gezag van de rector magnificus, prof.dr. P.van der Leeden, voor een commissie aangewezen door het college van dekanen in het openbaar te verdedigen op vrijdag 15 september 1978 te 16.00 uur

door

JACOB ZWART

geboren te Velsen

DRUK: WIBRO HELMOND

DIT PROEFSCHRIFT IS GOEDGEKEURD
DOOR DE PROMOTOREN:

Prof. dr. G.C.A. Schuit

Dr. ir. A.L. German

Aan Joke

CONTENTS

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CHAPTER 1

INTRODUCTION

Heterogenizing homogeneous catalysts

In the last decade, attachment of homogeneous catalysts to polymeric or inorganic carriers has received considerable attention. It is recognized that heterogenizing catalysts may offer the opportunity to retain the advantages of high activity and selectivity inherent for homogeneous catalysts and, at the same time allow ready recovery which is the great advantage of heterogeneity. However, apart from these technological advantages which have received most attention, attachment to a support may also have *mechanistic consequences e.g.*:

- Stabilization of catalytic species which normally undergo self-aggregation may occur, resulting in a consequent modification of kinetics, mechanism and/or selectivity.
- The support is essentially a ligand competing for available coordination sites of the catalyst. Actually, in most cases at least one coordination site is used for anchoring the catalyst to the support. There is no doubt, the ligand properties of the support will have their influence on the catalytic operation.
- Topological effects will result from attachment of the catalyst to a support and will have repercussions as to such features as stereospecificity and selectivity.
- The support offers a micro-environment to the catalyst and this may be utilized to create bifunctional or even multifunctional systems by appropriate choice of the chemical groups to be introduced into the

support.

The investigation described in this thesis is mainly concerned with the mechanistic effects connected with polymer attachment of a catalyst (in our case cobalt-phthalocyanine). After presenting a survey of the main literature referring to catalyst attachment, a more detailed description of the object of this investigation will be given.

Survey of the literature on supported catalysts

Haag and Whitehurst, at the Mobil Oil Laboratories, have been pioneers in the field of heterogenizing homogeneous catalysts for industrial use. Salts of $Pd(NH_3)_4^{2+}$ with polymeric counterions were used as catalysts in the insertion reaction of carbonmonoxide with allylchloride [1]. The authors also prepared catalysts for hydrogenation [2] and hydroformylation [3] reactions based on rhodium complexes attached to polymer-bound phosphine groups, which is a group of catalysts currently receiving wide attention [4]. A systematic survey on the subject of heterogenizing homogeneous catalysts is given by Bailar [5]. In most cases, specific activity or selectivity are not severely influenced by polymer attachment. However, Grubbs *et al.* [6] reported on a polystyrene attached titanocene catalyst used for the hydrogenation of olefins with an appreciably enhanced activity compared with the homogeneous counterpart (a factor 25-120), the increase of activity being attributed to a matrix induced stabilization of mononuclear species which are prevented to polymerize towards unreactive aggregates.

Those systems involving metal complexes attachted to *soluble* polymers with a variety of functional groups [7] are the most interesting from a mechanistic point of view. Besides steric effects governed by the conformation and density of the polymer-ligand chain, environmental effects exerted by the polymer domain can play an important role. In some cases, the use of soluble complexes has led to a marked increase of the reactivity because of a high local substrate concentration and/or the improved complexing ability due to the coiling up of the polymer together with electrostatic effects [8-10]. Recently, an excellent review appeared covering the extensive work of Tsuchida and coworkers [11], a leading group in this field of chemistry. The authors demonstrate that much progress has already been achieved in the qualitative and quantitative understanding of the relationship between the chemical function and the effects of a polymer chain in modifying catalytic complexes. The results clearly show that polymer-metal complexes can be developed exhibiting characteristic features normally encountered in enzyme chemistry only.

Aim and structure of this thesis

In this thesis we wish to investigate polymer attached cobalt-phthalocyanines (CoPc) applied as catalysts in the oxidation of mercaptans (RSH) by oxygen, carried out in aqueous media. Application of a cross-linked polymer as the carrier will enable to study the effects of *immobilization* of the catalytic species, possibly resulting in a stabilization of reactive intermediates against dimerization or aggregation.

The catalytic oxidation process is appreciably facilitated by addition of alkaline base generating the thiolate (RS^-) anion which is the species susceptible to the oxidation reaction (producing disulfide RSSR). This particular reaction, therefore, offers the opportunity to develop a *bifunctional* catalyst, *i.e.* a polymeric system not only containing the attached CoPc complex but also the basic groups required to activate the mercaptan (through its partial conversion into RS^-). In view of these considerations, soluble polymers containing amine groups will be used as a carrier for the CoPc catalyst. The catalytic system thus obtained will be applied in the absence of alkaline base to allow assessment of its bifunctionality.

The literature dealing with the catalytic properties of polymer attached metalloporphyrins or phthalocyanines in the autoxidation of mercaptans is rather scarce. However, industrial research focussing on the removal of mercaptans from cracked gasolines (sweetening) has led to a number of patents involving the use of supported metallophthalocyanines as catalysts [12-14]. To our knowledge, only Rollmann [15] introduced proton acceptor sites into the carriers in order to obtain bifunctional catalysts. These catalysts appeared to be active in the absence of alkaline base when used in a medium of 1 M benzene in hexane, but a rather rapid ageing restricted their applicability.

Nowadays, polymer-attached metalloporphyrins receive wide attention because of their ability to mimic the biological oxygen carriers. In some cases, excellent results were obtained on the reversible oxygenation of attached ferroporphyrins at room temperature, even when using water-soluble polymers as carriers [16, 17].

The cobalt complexes of porphyrins and phthalocyanines also show the ability of binding oxygen and, therefore, we expected that oxygen adducts of CoPc could play a role during the catalytic oxidation reaction. Preliminary results indeed gave evidence of the formation of oxygen adducts during the oxidation. Hence, an ESR study was undertaken to examine the conditions leading to the formation of mononuclear or binuclear oxygen adducts (chapter 2). Investigations by ESR of a CoPc catalyst bound to a cross-linked poly(acrylamide) matrix, revealed that the formation of binuclear oxygen adducts is appreciably hindered due to the polymer matrix. This feature probably plays an important role as to the enhanced activity shown by the polymer-attached catalyst (chapter 3).

Bifunctional catalysts were prepared by using polymers with incorporated amine groups, as the carrier for CoPc. We will demonstrate that these catalysts are extremely active in the absence of alkaline base (chapter 4 and 5). Catalytic systems with improved resistance against ageing are presented in chapter 5.

An investigation into the mechanism of oxidation of mercapto-ethanol catalyzed by the conventional NaOH/CoPc system will provide a better understanding of the enhanced activity observed for the polymer-attached systems (chapter 6). Finally, an attempt will be made to place all the results in context (chapter 7).

Part of this thesis was published already or has been submitted for publication, namely:

- Chapter 2: J. Zwart and J.H.M.C. van Wolput,
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- Chapter 3I: T.A.M.M. Maas, M. Kuijer and J. Zwart
  J. Chem. Soc. Chem. Comm., (1976) 86.
- Chapter 3II: J. Zwart and J.H.M.C. van Wolput,
  submitted for publication in J. Mol. Cat.
- Chapter 4: J. Zwart, H.C. van der Weide, N. Bröker,
  C. Rummens, G.C.A. Schuit and A.L. German,
  J. Mol. Catalysis, 3 (1977'78) 151.
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CHAPTER 2

AN ESR STUDY ON THE REACTION OF COBALT PHTHALOCYANINES WITH AMMONIA AND DIOXYGEN

Summary

The interaction of cobalt phthalocyanine with ammonia and oxygen in solutions of DMF was studied and the products investigated by ESR. Both mono- and bis-NH_3 adducts were prepared and characterized by their ESR signals showing the appropriate ^{14}N s.h.f. splitting. Admittance of air results in the formation of the monomeric 1:1 O_2 adduct identified by its characteristic ESR signal. The thermal stability of this 1:1 O_2 adduct is surprisingly high presumably because of the stabilizing effect of the highly polar solvent (DMF) combined with the strong Lewis base character of the axial coordinated base (NH_3). An irreversible loss of ESR signal of the 1:1 O_2 adduct is correlated with formation of the binuclear oxygen adduct, as found by optical spectroscopy; the rate of this reaction was shown to depend on the ammonia concentration. During the process of formation of the binuclear O_2 adduct, a narrow $g \sim 2$ signal was observed assigned to oxidation of the phthalocyanine ring to a cation radical.

1. Introduction

Several reviews on dioxygen-metal complexes have appeared, recently [1-5], and those concerning cobalt Schiff-bases [3, 4] and cobalt porphyrins [5] appear particularly interesting from a point of view of biological relevance [6]. The activation of the coordinated dioxygen was discussed by

Henrici-Olivé and Olivé [7], Valentine [8], and Wilkins [9].

It is currently accepted that the reactions involved in the oxygenation of planar cobalt complexes, are:

$$\mathrm{CoP + L \rightleftharpoons L.CoP} \tag{1}$$

$$\mathrm{L.CoP + L \rightleftharpoons L_2.CoP} \tag{2}$$

$$\mathrm{L.CoP\ .\ O_2 \rightleftharpoons L.CoP.O_2}\quad \text{(1:1 } \mathrm{O_2} \text{ adduct)} \tag{3}$$

$$\mathrm{L_2.CoP + O_2 \rightleftharpoons L.CoP.O_2 + L} \tag{4}$$

$$\mathrm{L.CoP.O_2 + L.CoP \rightleftharpoons L.CoP.O_2.CoP.L}\ \text{(2:1 } \mathrm{O_2} \text{ adduct)} \tag{5}$$

with P = porphyrin, Schiff-base or phthalocyanine and
L = a Lewis base.

Preliminary oxygenation experiments carried out with cobalt Schiff-base complexes, practically in all cases gave rise to dimeric μ-peroxo complexes (2:1 O_2 adducts).

Later on Floriani and Calderazzo [10], and the groups of Basolo [11] and Hoffman [12] were able to prepare a series of monomeric dioxygen adducts (1:1 O_2 adducts). The mode of dioxygen bonding (bent end-on coordination) followed from magnetic and ESR measurements [12].

Considerable interest has recently been shown in cobalt porphyrin complexes, which allow formation of mononuclear oxyge adducts at low temperature and therefore can serve as models for biological oxygen carriers. They have been studied by Walker [13, 14] using ESR spectroscopy. The thermodynamics of the equilibria (1)-(4) have been investigated using ESR techniques and optical spectroscopy [15-17]. With respect to reaction (5) - the formation of a binuclear dioxygen adduct - the literature data are not unanimous. Yamamoto and Kwan [18] concluded that after oxygenation at ambient temperature, only binuclear dioxygen adducts were formed, while Stynes *et al.* [19] were able to prepare the monodioxygen adduct only by oxygenation at low temperature. However, Walker [15] reported on a quite stable 1:1 O_2 adduct at ambient temperature, its ESR signal disappearing only slowly. The decay was ascribed to formation of the 2:1 O_2 adduct.

The literature dealing with cobalt phthalocyanines and their reactions with base and oxygen, is far less extensive. None the less, they are of great interest as model systems of biological oxygen carriers. Moreover, cobalt phthalocyanines have shown to be quite efficient oxidation catalysts [20]. They have been used as catalysts in the autoxidation of ascorbic acid [21], cysteine [22], mercapto-ethanol [23], hydrazine [24], and hydroxylamine [25]. During these oxidation reactions, dioxygen adducts of cobalt phthalocyanine seem to play an important role. Because of this paucity of data concerning cobalt phthalocyanines, we have studied their interaction with base and oxygen (reactions (1)-(5)) by ESR and optical spectroscopy techniques. Special attention will be given to the conditions which lead to formation of the 2:1 O_2 adducts

2. Experimental

Dimethylsulfoxide (DMSO)(Merck, p.a.), methanol (Merck, p.a.), and N,N-dimethylformamide (DMF) (Fluka, p.a.) were used as received. Ammonia (Matheson) was purified from oxygen before use by bubbling the gas through a highly oxygen sensitive solution of cysteine/CoTSPc in DMF.

Cobalt(II) 4, 4', 4'', 4'''-tetrasulfophthalocyanine (CoTSPc) was prepared according to the procedure described by Weber and Busch [26].

Anal. Clcd. for $C_{32}H_{12}N_8O_{12}S_4Na_4.7H_2O$ (M = 1105): C, 34.75; H, 2.17; N, 10.13; Na, 8.33; Co, 5.34. Found: C, 34,68; H, 2.06; N, 10.31; Na, 8.1; Co, 5.1.

Cobalt(II) 4, 4', 4'', 4'''-tetranitrophthalocyanine ($CoTNO_2Pc$) was prepared according to the same procedure [26], making use of 4-nitrophthalic acid as agent.

Anal. Calcd. for $C_{32}H_{12}N_{12}O_8Co$ (M = 751): C, 51.13; H, 1.6; N, 22.37; Co, 7.8. Found: C, 49.04; H, 2.0; N, 21.54; Co, 6.5.

Cobalt(II) 4, 4', 4'', 4'''-tetraaminophthalocyanine ($CoTNH_2Pc$) was prepared by reduction of $CoTNO_2Pc$: $CoTNO_2Pc$ (10.4 g; 0.014 mole) was suspended in 300 ml dist.H_2O; $Na_2S.9H_2O$ (50g; 0.2 mole) was added to the suspension with stirring, continued during 8 hrs at 50°C. The product was obtained by filtration and purified by boiling in 400 ml 5%-NaOH during 1 hr. The resulting solid was repeatedly washed with boiling H_2O (dist.) until colorless filtrate. The product was dried overnight *in vacuo* over P_2O_5 (110°C, 5mm Hg); yield 80%. *Anal.* Calcd. for $C_{32}H_{20}N_{12}Co$ (M = 631): C, 60.85; H, 3.17; N, 26.59; Co, 9.35. Found: C, 59.78; H, 3.01; N, 25.80; Co, 8.5.

Procedure: For ESR measurements, typically, 1 ml 2 x 10^{-3}M of CoPc solution was used. Samples were freed from oxygen by degassing on a vacuum line (freeze-pump-thaw method). After degassing, a part of the solution was introduced into ESR quartz tubes connected to the vacuum line by standard-taper joints and provided with vacuum stop cocks. Ammonia adducts were prepared by admittance of the appropriate amount of NH_3-gas (purified according to the above ascribed procedure) to 1 ml of degassed solution. Oxygenation was carried out by introduction of air and subsequent mixing. Optical spectra were recorded parallel with ESR measurements. Use was made of 10 ml 10^{-4}M CoPc solution in order to allow recording of optical spectra in a 1 mm cell joint to the vacuum line.

Apparatus: Use was made of a Varian E-15 ESR spectrometer with E-101 microwave bridge (X-band) and a V-4540 variable temp. controller.

Field measurements were carried out with a nuclear resonance fieldmeter (AEG); a microwave frequency converter (HP2590B) and auxilary frequency converter (HP5253B) served for frequency measurements.

A Unicam UV-spectrophotometer (SP-800D) was used for optical measurements.

3. Results

According to the results reported by Smith *et al.* [27] no signal is detectable for cobalt tetrasulfophthalocyanine (CoTSPc) in frozen aqueous solution (T = -140°C). The authors attribute this to the formation of dimers or even polymers in water. The occurrence of dimers has also been reported by Gruen and Blagrove [28], using visible sprectroscopy. The monomer/dimer equilibrium was studied in more detail by Pratt

TABLE 1

ESR parameters of cobalt(II)-phthalocyanines

Compound	Conditions	$g_{\parallel}$	$g_{\perp}$	$10^4 \lvert A_{\parallel} \rvert$ cm^{-1}	$10^4 \lvert A_{\perp} \rvert$ cm^{-1}
CoTSPc	DMSO/-170°C	2.008	2.27	98	0
CoTSPc[x]	DMSO/-196°C	2.005	2.26	98	21
CoTPPS[xx]	DMSO-H_2O/-196°C	2.05	2.31	95	0
CoTSPc	MeOH/-140°C	2.007	2.26	94	0
CoTSPc[xxx]	MeOH/-175°C	2.0068	2.27	107	–[+]
CoTSPc	DMF/-140°C	2.006	2.26	97	0
CoTNH$_2$Pc	DMF/-100°C	2.006	2.40	115	67
CoTPPS[xx]	DMF-H_2O/-196°C	2.040	2.41	95	43

[x] From Ref. [32]

[xx] From Ref. [35]; CoTPPS: cobalt(II)tetraphenylporphyrin-tetrasulfonate

[xxx] From Ref. 34

[+] Not mentioned

et al. and Reynolds and Kolstad [29, 30]. From these studies it became apparent that water is the only solvent which promotes formation of dimeric species.

Indeed, our measurements in frozen solutions of DMSO, DMF, or methanol, gave rise to clear ESR signals of CoTSPc and CoTNH$_2$Pc, the parameters of which are given in Table 1. We found the observed spectra in DMSO and, particularly, in DMF to be superpositions of the signals of cobalt phthalocyanine and of the 1:1 O_2 adduct. This agrees well with reported oxygenation at low temperature for cobalt porphyrins [16, 31] in DMF solutions due to axial ligation of this solvent. The additional signal of 1:1 O_2 adduct can be eliminated by evacuation.

The resulting CoTSPc signal in DMF, DMSO or methanol, is very similar to that reported by Rollmann and Chan [32].

It should be noted that the listed values for $|A_{\perp}|$ (0×10^{-4} cm^{-1}) differ from that reported by Rollmann and Chan (21×10^{-4} cm^{-1}). Our assignment is based on a computer simulation carried out by Smith *et al.* [27] for this particular spectrum, which gave excellent fit using $|A_{\perp}| \sim 0$, while the parameters of Rollmann and Chan gave no satisfactory results. The spectrum of CoTNH$_2$Pc (Fig. 1) is quite different from that of CoTSPc and resembles the type B spectrum as designated by Smith *et al.*, an example of which is given in Table 1 (*see* CoTPPS). Both types of spectra seem to arise from $^2A_1$ ground state, with the unpaired electron residing in the d_{z^2} orbital [33].

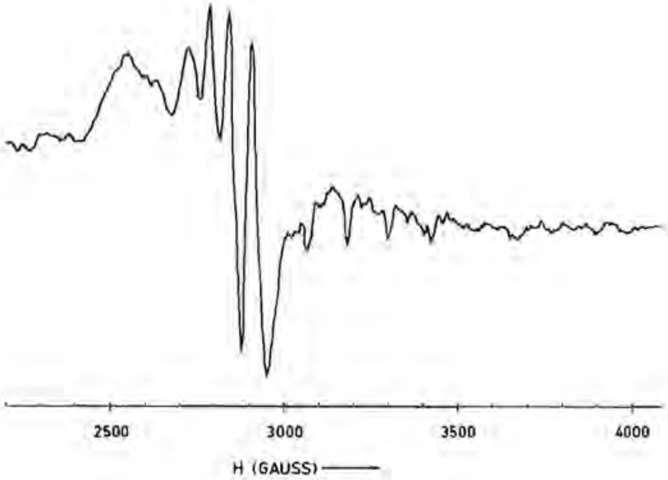

Fig. 1. ESR spectrum of CoTNH$_2$Pc in frozen degassed DMF solution (T = -140°C, microwave frequency: 9118 MHz).

3.1 Reactions with base (reaction (1) and (2))

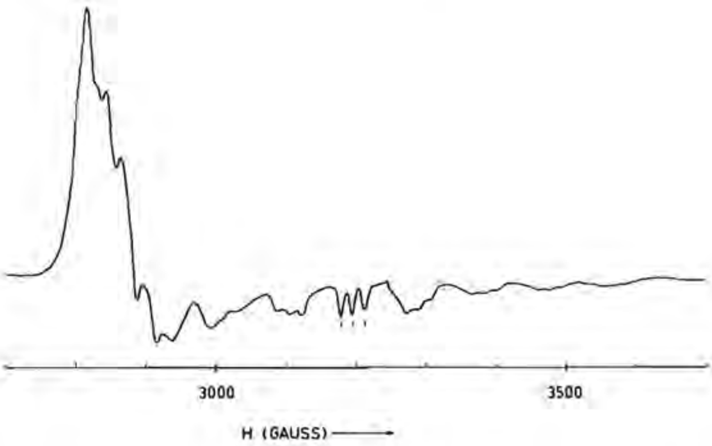

Fig. 2. ESR spectrum of CoTSPc(NH_3)$_1$ in frozen degassed DMF solution (T = -140°C, microwave frequency: 9107 MHz).

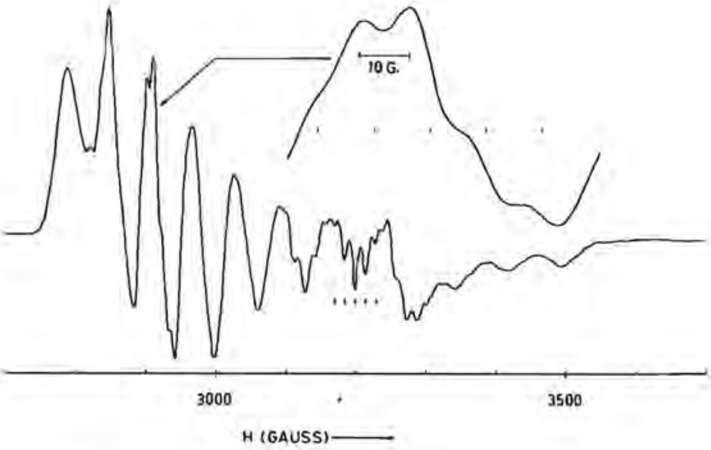

Fig. 3. ESR spectrum of CoTSPc(NH_3)$_2$ in frozen degassed DMF solution (T = -140°C, microwave frequency: 9107 MHz).

TABLE 2

ESR parameters of five- and six-coordinated cobalt phthalocyanines

Compound	conditions	$g_{\parallel}$	$g_{\perp}$	$10^4 \lvert A_{\parallel} \rvert$ cm^{-1}	$10^4 \lvert A_{\perp} \rvert$ cm^{-1}	$10^4 \lvert A_{N_{\parallel}} \rvert$ cm^{-1}	$10^4 \lvert A_{N_{\perp}} \rvert$ cm^{-1}
$CoTSPc(NH_3)_1$	DMF/-120°C	2.006	2.28	87	0	16	30^{x}
$CoTSPc(py)_1{}^{+}$	DMSO/-196°C	2.005	2.22	86	31	15	$-^{xx}$
$CoPc(4\text{-}Mepy)_1{}^{++}$	CH_2Cl_2/–^{xxx}	2.005	2.32	98	15	16	$-^{xx}$
$CoTSPc(NH_3)_2$	DMF/-120°C	2.012	2.16	70	62	15	11
$CoTSPc(py)_2{}^{+}$	DMSO/-196°C	2.006	2.17	76	52	14	12
$CoPc(4\text{-}Mepy)_2{}^{++}$	CH_2Cl_2/–^{xxx}	2.015	2.25	77	12	14	$-^{xx}$

x Tentative assignment

xx Not reported

xxx Frozen solution

\+ From Ref. [32]

++ From Ref. [36]

For complete oxygenation of square planar cobalt complexes an additional base - for instance a nitrogen base as pyridine or imidazole and derivatives [15-17] - is required. Following Pratt *et al.* [34], who demonstrated the reversible formation of the 1:1 O_2 adduct in methanol, we have chosen for ammonia as a base. By rigorous exclusion of dioxygen from the system, we prepared both the mono- and bis-NH_3 adduct of CoTSPc in DMF solution. Both compounds were characterized by their ESR spectrum recorded at low temperature in frozen solution (Table 2).

The mono-NH_3 adduct (Fig. 2) could be obtained using NH_3/Co ratios in solution ranging from 2 to 10, the lowest value being indicative of the strong affinity of NH_3 for the cobalt center in CoTSPc. The base can be eliminated by evacuation, giving rise to the ESR signal of base-free CoTSPc. The characteristic ^{14}N superhyperfine splitting in the parallel region is quite distinct. By visual inspection, the splitting in the perpendicular region is ascribed to ^{14}N s.h.f. splitting, too.

Application of NH_3/CoTSPc mixtures in DMF in the ratio 50/1 - 400/1, resulted in the formation of CoTSPc$(NH_3)_2$, as proven unambiguously by the characteristic quintuplet-splitting in its ESR signal. This can be observed quite distinctly both in the parallel region and in the perpendicular region, as shown in Fig. 3. The ESR parameters are similar to those reported by Rollmann and Chan [32] for the corresponding bis-pyridine adduct (Table 2). The original spectrum was restored upon evacuation.

3.2 Formation of dioxygen complexes (reactions (3)-(5))

Admittance of molecular oxygen or air to the solution of base-adduct resulted in the complete disappearance of the original signal. At the same time, another well known signal arises attributed to formation of the 1:1 O_2 adduct. ESR measurements were performed in frozen DMF solutions as well as in fluid solutions. The results, listed in Table 3, are in agreement with those reported for 1:1 O_2 adducts of CoTSPc in methanol [29], of cobalt porphyrins [14, 31], and of cobalt Schiff-bases [12, 37]. The actual value of the isotropic Co

TABLE 3

ESR parameters of 1:1 O_2 adducts of cobalt phthalocyanines

Compound	Conditions	$g_{\parallel}$	$g_{\perp}$	$10^4 \lvert A_{\parallel} \rvert$ cm^{-1}	$10^4 \lvert A_{\perp} \rvert$ cm^{-1}
$CoTSPc(NH_3)O_2$	DMF/-140°C	2.075	2.006	15	8.2
$CoTSPc(NH_3)O_2^{x}$	MeOH/-175°C	2.075	2.004	14.9	7.9
$CoTSPc(DMF)O_2$	DMF/-120°C	$-^{xx}$	2.006	$-^{xx}$	12.8
$CoTNH_2Pc(NH_3)O_2$	DMF/-140°C	2.080	2.008	15	8.3
		g_{iso}			10^4 A_{iso} cm^{-1}
$CoTSPc(NH_3)O_2$	DMF/-70°C	2.024			9.4
$CoTSPc(NH_3)O_2^{x}$	MeOH/-100°C	2.025			9.9
$CoTSPC(DMF)O_2$	DMF/-70°C	2.022			9.4

x From Ref. [34]

xx Not resolved.

h.f.s. of the 1:1 O_2 adduct appears to decrease in the order $CoSB(py)O_2$ > $CoPor(py)O_2$ > $CoPc(NH_3)O_2$ (12.96 [12], 11.21 [31], 9.9 [34] and 9.4 [this work]), indicating a lower spin density on the cobalt nucleus for the phthalocyanine system.

The oxygen-free cobalt phthalocyanine can be recovered from the 1:1 O_2 adduct in two different ways; *i.e.*, by means of direct evacuation (method 1) or, alternatively, by open air contact during about one hour (method 2). In both cases, the solved ammonia will evaporate, giving rise to dissociation of the 1:1 O_2 adduct. In the case of open air contact, the deoxygenation will not be complete, owing to axial coordination by the solvent (DMF). In order to achieve complete recovery of the oxygen-free CoTSPc signal, the liquid requires subsequent degassing by evacuation. When using method 2, no losses of signal intensity are observed, however, direct evacuation (method 1) leads to slight losses.

If the ammonia is prevented to evolve from the aerated solution by closing the stop cock, as expected, no regeneration of the original CoTSPc signal takes place.
However, when keeping the solution at room temperature, a loss of signal intensity of the 1:1 O_2 adduct is detected. The rate of this signal loss becomes faster with increasing concentration of ammonia in the solution. The time required to reduce signal intensity to half its original value ($\tau_{\frac{1}{2}}$) may provide an indication of the rate dependence of this decay process.
Variation of the ratio NH_3/CoTSPc in the aerated solution has a remarkable effect on the value of $\tau_{\frac{1}{2}}$; *i.e.*, ratios NH_3/CoTSPc of 2, 20, and 400 correspond with $\tau_{\frac{1}{2}}$ values of approximately 16 hrs, 1 hr and 1 minute, respectively. Obviously an irreversible transformation into a diamagnetic species has taken place, as this particular loss of signal intensity is connected with an equal loss of signal for the recovered product (CoTSPc), upon evacuation.

The observed transformation process is accompanied by a change in colour of the solution from blue to green. The resulting *optical* spectrum differs appreciably from the spectra recorded for the mononuclear species as shown in Fig. 4 and 5. Evidence of formation of the binuclear dioxygen adduct during this transformation process was obtained by making use of results on oxygenation of CoTSPc reported by Wagnerová *et al.* [38]. These authors demonstrated, from manometric measurements of oxygen absorption in alkaline media, that oxygenation resulted into the formation of a product with a stoichiometry $Co/O_2 = 2/1$ (*i.e.* reaction 5). Unfortunately, only the low-energy bands of the 2:1 O_2 adduct were depicted. It should be noted, however, that in our measurements distinct band shifts are observable in the NUV-region during the formation of the diamagnetic species (*see* Fig. 4). Therefore, we prepared the binuclear oxygen adduct in aqueous media according to Wagnerová *et al.* [38]

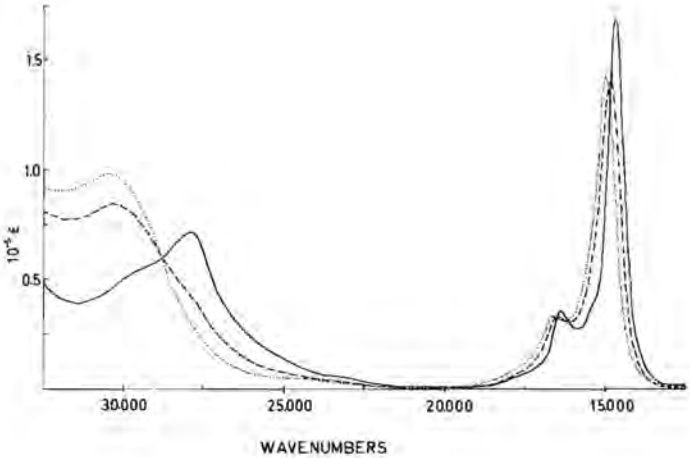

Fig. 4. Optical spectra of CoTSPc and its dioxygen adducts in DMF solution; ......CoTSPc,
------CoTSPc(NH_3)O_2,
———(NH_3)CoTSPc.O_2.CoTSPc(NH_3).

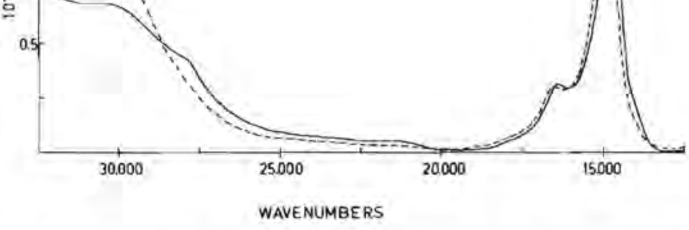

Fig. 5. Optical spectra of the mono- and bis-NH_3 adduct of CoTSPc. The solutions were degassed prior to adduct formation; ------CoTSPc(NH_3)$_1$,
———CoTSPc(NH_3)$_2$.

and compared spectra also in the NUV-region. The optical spectra thus obtained in aqueous media were entirely similar to that observed for our product in DMF. Accordingly, the decay of signal observed in our measurements is attributed to the formation of a binuclear oxygen adduct (reaction 5).

3.3 Thermal stability of the 1:1 O_2 adduct

By cooling a solution of CoTSPc(NH_3)O_2 in DMF until -60°C no change in optical spectrum could be observed, apart from a slight rise in intensity of the major absorption band, typical of recordings at lower temperature. However, at -60 C, ESR spectra are fully consistent with the presence of the 1:1 O_2 adduct. Therefore, These results seem to suggest that the mononuclear 1:1 O_2 adduct under investigation is stable even at room temperature.

In order to obtain further evidence on the stability of CoTSPc(NH_3)O_2, we compared the thermal stability of the 1:1 O_2 adducts with NH_3 and with DMF as axial ligand by monitoring their ESR signals. Recordings of the two ESR signals at -140°C show that the intensity of the signal of CoTSPc(NH_3)O_2 is about twice that of CoTSPc(DMF)O_2. In the latter case, there is an additional signal ascribed to oxygen-free CoTSPc. After raising the temperature above the melting point of DMF, we observe (T = -60°C) that under otherwise comparable conditions the intensity of the signal of CoTSPc(NH_3)O_2 is now about a factor of 50 larger than of CoTSPc(DMF)O_2.

With further raise of temperature also the intensity of the CoTSPc(NH_3)O_2 signal diminishes (factor 15 going from -60 to -20°C), but no other signals could be detected, as might be expected if dissociation of the complex had taken place. Hence, this observed signal reduction may be ascribed to changing specific ESR phenomena, as for instance relaxation effects and dielectric losses occurring in the liquid phase, and not to an inherent instability of the CoTSPc(NH_3)O_2 species.

4. Discussion

4.1 Characterization of products

As shown above the interaction of cobalt tetrasulfophthalocyanine (CoTSPc) with ammonia in DMF as solvent, gives rise to reversible formation of both mono- and bis-NH_3 adducts, depending on the amount of NH_3 used. Both adducts could unambiguously be characterized by ESR spectroscopy, from the appropriate ^{14}N superhyperfine structure exhibited in the parallel region of the signals (Fig. 2 and 3). In addition, the signal of CoTSPc$(NH_3)_2$ shows a clearly resolved ^{14}N superhyperfine splitting due to interactions with two nitrogen nuclei in the perpendicular region. For the mono-NH_3 adduct assignment of the observed splitting in the perpendicular region is less obvious.
We tentatively suggest that also in this case, the splitting is due to ^{14}N s.h.f. splitting.

The difference between ESR signals of CoTSPc(NH_3) and CoTSPc$(NH_3)_2$ is not only revealed by the different ^{14}N s.h.f. splitting observed in the parallel region, but, in addition, striking differences appear in the overall picture of the signals as is obvious from comparison of Fig. 2 and 3. The observed transformation of the signal, going from 5-coordination (mono-NH_3 adduct) to 6-coordination (bis-NH_3 adduct) is quite similar to that reported for cobalt porphyrins in frozen toluene glasses [39].
Upon admittance of oxygen to the solution (reaction (3) and (4)), both 5-coordinate and 6-coordinate ammonia complexes allowed reversible formation of 1:1 O_2 adduct. The ESR signal of the 1:1 O_2 adduct is consistent with a predominantly axial symmetry of the *g*-tensor, showing an overall picture very similar to that already reported [34].

In oxygenation experiments with planar cobalt complexes usually also the formation of the dioxygen bridged dimer (2:1 O_2 adduct) is reported [2-4]. In our case, formation of a diamagnetic species from the 1:1 O_2 precursor was indeed observed, its rate being strongly dependent on the amount of base (NH_3) present. Examination of its *optical* spectrum lends support to the suggestion that the observed behaviour may be ascribed to the formation of the 2:1 O_2 adduct (reaction 5). The optical spectrum proved to be essentially the same as that of the 2:1 O_2 adduct as prepared in alkaline aqueous solutions according to the method given by Wagnerová *et al.* [38]. In addition, compared with our observations in DMF a similar dependence of the rate of formation of the 2:1 O_2 adduct on the amount of base, present in the aqueous solution, was reported by these authors.

The high intensity of the low-energy band is quite typical of the 2:1 O_2 adduct, but even more characteristic are changes monitored in the *N-UV* region upon formation of the 2:1 O_2 adduct (*see* Fig. 4), which allow clear distinction to be made. The intense *N-UV* band (ν = 27.900 cm^{-1}, ε = 0.65 x 10^5 M^{-1} cm^{-1}) is unique for the 2:1 O_2 adduct, but it should be noted that also the 1:1 O_2 adduct and bis-NH_3 adduct show a shoulder in this region. Hence, we suggest that this feature may be specific for 6-coordinate complexes.

4.2 Thermal stability of 1:1 O_2 adduct

ESR measurements revealed that the 1:1 O_2 adduct is unusually stable; even at temperatures as high as -20°C no evidence for dissociation of the adduct could be obtained. Usually, cobalt porphyrins bind oxygen much weaker than cobalt Schiff-bases [17], therefore the majority of reported 1:1 O_2 adducts of cobalt porphyrins could only be observed at fairly low temperatures ($T \sim -70^{\circ}C$).

The observed relatively high stability may partly be ascribed to the effect of the strongly polar solvent (ε_{DMF} = 37), which allows stabilization of the polar $Co(III)-O_2^-$ bonding.

Similar effects were already reported for cobalt porpyrins [31], explained [40] as due to a more favourable enthalpy for oxygen binding, with DMF as solvent. In addition, stability of 1:1 O_2 adducts appears to rise with use of stronger Lewis bases [11, 16]; hence, axial coordination of NH_3 (pK_a = 9.25) will promote oxygen affinity of the complex.

4.3 Formation of binuclear oxygen adduct

The observed loss of intensity of the ESR signal of the 1:1 O_2 adduct, ascribed to formation of the 2:1 O_2 adduct (reaction (5)), has been shown to be strongly dependent on the concentration of NH_3 in the solution. Moreover, upon evacuation of the solution, signal losses were also observed with use of relatively low amounts of NH_3. This can be interpreted, assuming that not the absolute concentration of NH_3 is rate determining, but rather the ratio NH_3/O_2 in the solution. During the process of evacuation this ratio will tend to rise, because of the high affinity of the solvent (DMF) to NH_3.

These results may be qualitatively understood, when taking into account the equilibrium (4):

$$\underset{\text{(I)}}{\mathrm{NH_3} \rightarrow \mathrm{Co} - \mathrm{O_2}} + \mathrm{NH_3} \rightleftharpoons \underset{\text{(II)}}{\mathrm{NH_3} \rightarrow \mathrm{Co} \leftarrow \mathrm{NH_3}} + \mathrm{O_2} \qquad (4)$$

The formation of binuclear oxygen adduct involves the reaction of an oxygenated species (I) and an oxygen-free complex (II). Usually, the 5-coordinate complex is supposed to be reactive in the formation of the 2:1 O_2 adduct, but there are no reasons to believe that the 6-coordinate complex would be entirely unable to react.

Under typical oxygenation conditions, no evidence for the presence of oxygen-free NH_3 adducts could be obtained, using ESR spectroscopy. Hence, the majority of cobalt complexes is present in the oxygenated form (I), which is consistent with thermodynamic parameters for reaction (4), reported by Walker *et al.* [41] for similar porphyrin complexes. According to equilibrium (4), the concentration of oxygen-free complex can be raised by enhancement of the NH_3 concentration, or by lowering the O_2 concentration at constant NH_3 level. It is reasonable now, to assume that this shift in equilibrium, leading to a higher concentration of NH_3 adduct (II), will result in a higher rate of the formation of 2:1 O_2 adduct. Otherwise, when the solution of 1:1 O_2 adduct is in open contact with the air, then NH_3 will gradually evolve from the solution, while the O_2 concentration remains constant. Accordingly, the formation of 2:1 O_2 adduct will now be suppressed, as was in fact observed.

4.4 Character of intermediate species during formation of the binuclear oxygen adduct.

According to kinetic measurements, Stynes *et al.* [19] supposed that a reorganization within the 1:1 O_2 adduct of cobalt porphyrins occurs, prior to the coupling reaction (6):

$$L \longrightarrow \overset{|}{\underset{|}{Co}} - O_2 \xrightarrow{k^*} \left[L \longrightarrow \overset{|}{\underset{|}{Co}} - O_2 \right]^* \qquad (6)$$

They speculated about the nature of this process; it could be related to a charge transfer process $Co \longrightarrow O_2$, which results in an increased O-O bond length and a decrease in bond order, translated in going from a superoxo- to a peroxo-intermediate. However, the consequence of this will be, that oxidation of the cobalt porphyrin moiety will happen. This reasoning implicates an oxidation of the porphyrin ring, as oxidation of Co(III) to Co(IV) seems not probable. Moreover, one electron oxidations of metal porphyrins and phthalocyanines, resulting in the formation of cation radicals, are well known in the literature [42, 43]. In this connection, it should be noted that our ESR measurements give some evidence for the presence of an intermediate cation radical during the formation of 2:1 O_2 adduct.

As mentioned earlier, rapid conversion of the 1:1 O_2 adduct into the 2:1 O_2 adduct can be accomplished using relatively high amounts of NH_3 in the solution. Just before completion of this reaction the ESR spectrum shows the reduced signal of 1:1 O_2 adduct, but, additionally, a signal of narrow band width ($\Delta H \sim 10G$) with g-value in the free radical range ($g \sim 2.003$). Presumably, this $g \sim 2$ signal is also present in an earlier stage of the reaction, but then obscured by the intense signal of the 1:1 O_2 adduct.

It is known that metal cation radicals of phthalocyanines exhibit similar ESR signals [43]. Therefore, we suggest that the observed $g \sim 2$ signal may be assigned to an intermediate cation radical, which is formed by internal electron rearrangement, prior to the coupling process, consistent with ideas of Stynes *et al.* [19].

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CHAPTER 3

(I) ACTIVATION OF COBALT-PHTHALOCYANINE CATALYST BY POLYMER ATTACHMENT

Results

Recently, Rollmann [1] reported on the activity and stability of polymer-bonded metalloporphyrins for the oxidation of thiols. Some of them were effective catalysts, but during the reaction deactivation occurred. Our studies usually confirmed this but we now report a catalyst system which is both active and stable.

The active catalyst component is cobalt(II)-4, 4', 4'', 4'''-tetra-aminophthalocyanine (CoTNH$_2$Pc) prepared according to the method of Shirayaev *et al.* [2]. It was coupled by means of cyanuric chloride [3] to NH$_2$ groups of a polymer matrix. The polymers used were aminated [4] Merrifield[†] resin and Enzacryl AA[††]. The resulting catalysts can be represented as (I) and (II) *(see next page)*.

[†] Merrifield (Fluka) resin is a polystyrene cross-linked with 2% divinylbenzene and chloromethylated to give 3·5 mmol of CH$_2$Cl per g.

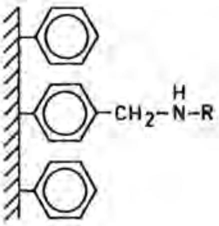
[††] Enzacryl AA (Koch-Light) is a cross-linked polyacrylamide with aniline-substituted acrylamide groups

TABLE 1

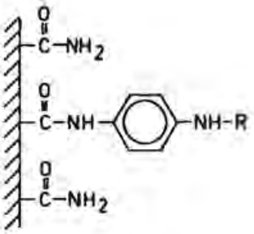
Activities of the catalysts

Catalyst	Support	Co/Mol(x 10^9)	Rate (ml min^{-1})	Specific Rate (ml min^{-1} μmol^{-1})	Relative rate
CoTSPc	-	100	3.4	34	1
(I)	Merrifield resin	763	2.3	3.02	0.089
(II)	Enzacryl AA	13	1.75	135	4.0
(II)[a]	"	13	2.6	200	5.88

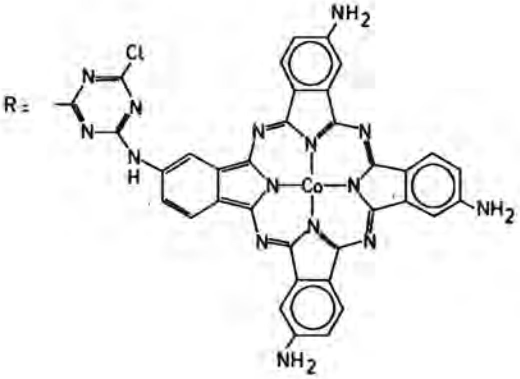
[a] This catalyst was ball-milled for 20 min immediately before use. Reaction conditions: 75 ml of H_2O per 6 mmol of NaOH, 1 ml ME, catalyst, 22°C, 1 atm of O_2, vigorous stirring.



catalyst I



catalyst II



The catalysts were tested for the oxidation of 2-mercaptoethanol (ME) by measuring the rate of oxygen consumption (equations 1 and 2).

$$4HSCH_2CH_2OH + 4OH^- \longrightarrow 4\,^-SCH_2CH_2OH + 4H_2O \qquad (1)$$

$$4\,^-SCH_2CH_2OH + O_2 + 2H_2O \longrightarrow 2HOCH_2CH_2S\text{-}SCH_2CH_2CH_2OH + 4OH^- \qquad (2)$$

In order to relate the performance of the polymeric catalysts to that of the corresponding soluble catalyst, we also studied aqueous solutions of cobalt-tetrasulphophthalocyanine (CoTSPc), which has proved to be one of the most active phthalocyanine catalysts for thiol oxidation [5]. The polymeric catalysts were powdered

TABLE 2

Activity in successive runs[a]

No.	Rate /ml min^{-1}	Uptake of O_2 after 10 min ml
1	2.9	27.6
2	2.7	25.2
3	2.8	26.6
4	3.0	28.5
5	2.9	28.4
6	3.0	28.9

[a] After each run the catalyst was filtered and washed with water in preparation for the next run. Reaction conditions: 75 mg of catalyst (I) in 75 ml of H_2O per 9 mmol of NaOH, 1 ml ME, 22°C, 1 atm of O_2.

before use[§]. Oxidation rates and catalytic activities relative to the soluble catalyst, and reaction contitions are given in Table 1.

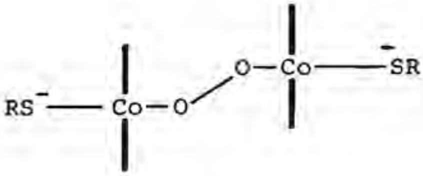
The catalysts were also tested for their stability in successive experiments. The results for catalyst (I) are given in Table 2. Similar results were obtained with catalyst (II).

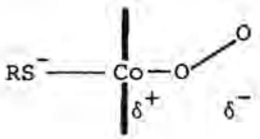
[§] catalysts (I) and (II) contained 0.06 and 0.21% Co, respectively. Because of the small amount of catalyst (II) necessary for an experiment, it was diluted by thoroughly mixing it with polystyrene powder (XAD-2, Rohm and Haas); the dilution factor for (II) was 15 and for ball-milled (II) was 75.

The data demonstrate the following: (a) the catalysts (I) and (II) do not show deactivation, (b) activity is highly dependent on the supporting polymer used; catalyst (II) is more active than the soluble analogue, and (c) ball-milling to reduce the catalyst particle size led to an increase in the activity, which indicates diffusion limitations and suggests that a further enhancement of activity would result from a reduction in the diffusion resistance.

The difference in activity between catalyst (I) and (II) is attributed to the difference in diffusion limitations, corresponding to the greater 'swellability' of the polyacrylamide in comparison to the polystyrene matrix. The reasons for the stability and the high activity of the catalysts are not clear at this stage.

Preliminary results show that the kinetics of oxidation with the soluble and insoluble catalysts are different. The order of reaction in substrate in the solution reaction is *ca.* 1, whereas in the heterogeneous system it is appreciably lower than 1, indicating michaelis-Menten kinetics[+].


(III)


(IV)

[+] Catalysts (I), (II) and ball-milled (II) had *KM* values of 19.2, 33.3, and 53.3 ml of ME per litre, respectively, and turn-over numbers of 1100, 70,000, and 153,000 mol of ME per mol of Co per min, respectively.

The reactive intermediate in the solution, accounting for almost the total amount of catalyst, has been found by spectral studies to be (III). Since such a dimer may be prevented from forming in the matrix because the groups are held apart from one another, it is possible that the higher activity of the polymers is a consequence of the presence of a single cobalt species (IV). Higher activity may be related to the more highly activated oxygen present in (IV).

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(II) CHARACTERIZATION BY ESR OF A POLYMER ATTACHED COBALT (II)-PHTHALOCYANINE CATALYST

Results

Resin bound transition-metal complexes currently receive wide attention because of their attractive catalytic properties [1, 2]. Application of rigid supports offers the opportunity to prepare catalysts with a distribution of active sites ensuring mononuclearity and retaining this distribution during the catalytic reaction. In those cases that deactivation of a catalyst is due to dimerization or aggregation of active sites, polymer attachment of the active metal complex may result in the formation of an unusually active catalyst. Thus, Grubbs *et al.* [3] demonstrated that by polymer attachment of a titanocene complex, the hydrogenation activity of the catalyst could be enhanced by a factor of 25-120.

Recently [4], we reported on a catalyst for the autoxidation of mercapto-ethanol, *viz.* Cobalt(II)- tetraminophthalocyanine ($CoPc(NH_2)_4$) covalently bonded to a cross-linked polyacrylamide carrier.+

+The carrier used was Enzacryl AA (Koch-Light), which is a porous granulate, consisting of cross-linked polyacrylamide with incorporated aniline substituents.
After coupling the $CoPc(NH_2)_4$ catalyst through its NH_2-ringsubstituent to the polymer by means of cyanuric chloride, the product was washed thoroughly with conc. H_2SO_4 to remove uncoupled catalyst. The resulting polymeric catalyst contains 0.21% Co.

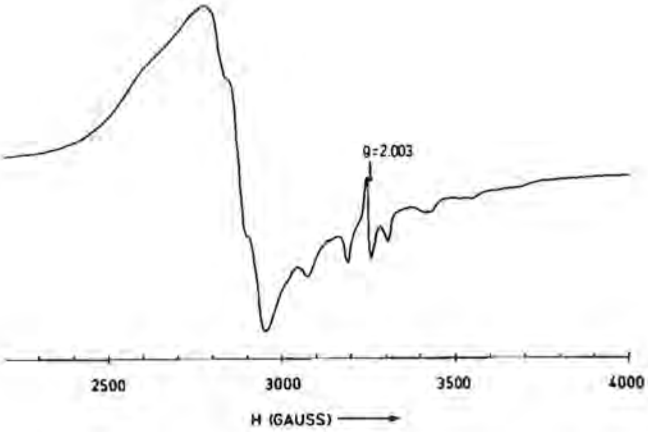


Fig. 1. ESR spectrum of polymer attached CoPc(NH_2)$_4$ catalyst suspended in water. Recorded at -140°C. Spectrometer settings: microwave frequency 9.11 GHz, power 50 mW, modulation amplitude 8 Gauss, receiver gain 1.25 × 10^2.

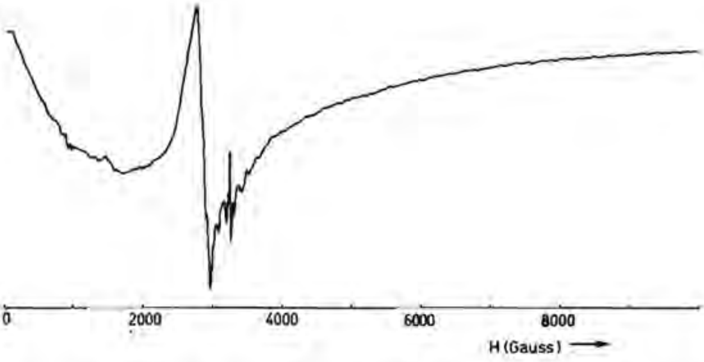
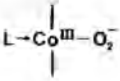
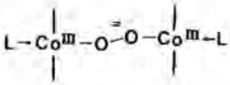


Fig. 2. Wide scan ESR spectrum of dry polymer attached CoPc(NH_2)$_4$. Recorded at -40°C. Spectrometer settings: microwave frequency 9.11 GHz, power 50 mW, modulation amplitude 8 Gauss, receiver gain 4 × 10^2.



$L \rightarrow Co^{III}-O_2^-$

(I)



$L \rightarrow Co^{III}-O\overset{=}{-}O-Co^{III} \leftarrow L$

(II)

For the polymer attached catalyst we found a significantly enhanced catalytic activity compared to its soluble polymer-free analogue. The enhanced activity was ascribed to the highly reactive mononuclear *superoxo*-complex (I), being operative in the matrix, whereas a relative deactivation occurred in solution due to formation of the less reactive dimeric *peroxo*-complex (II).

We now have found positive evidence for the supposed mononuclear distribution giving rise to enhanced activity. Characterization* of the polymer attached catalyst has been carried out by ESR spectroscopy.

ESR investigations of the polymeric catalyst powder or of a suspension of it in water, dimethylformamide (DMF), or conc. H_2SO_4 show well resolved ESR signals. In all cases, the signals are similar and comparable to the signal of a homogeneous solution of the catalytic component ($CoPc(NH_2)_4$) in DMF [5]. As an example, the ESR signal of the polymeric catalyst suspended in H_2O is presented (Fig. 1). The excellent resolution of the ^{59}Co h.f.s. exhibited in the parallel region provides striking evidence of the presence of isolated mononuclear cobalt centres. Some of the cobalt centres, however, are still engaged in site-site interactions as inferred from the broad back-ground signal (absent in the carrier) exhibited by the dry catalyst powder (Fig. 2). It should be noted that

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*Microprobe analysis revealed that metal concentration was uniformly distributed throughout the pumice-like polymer particles.

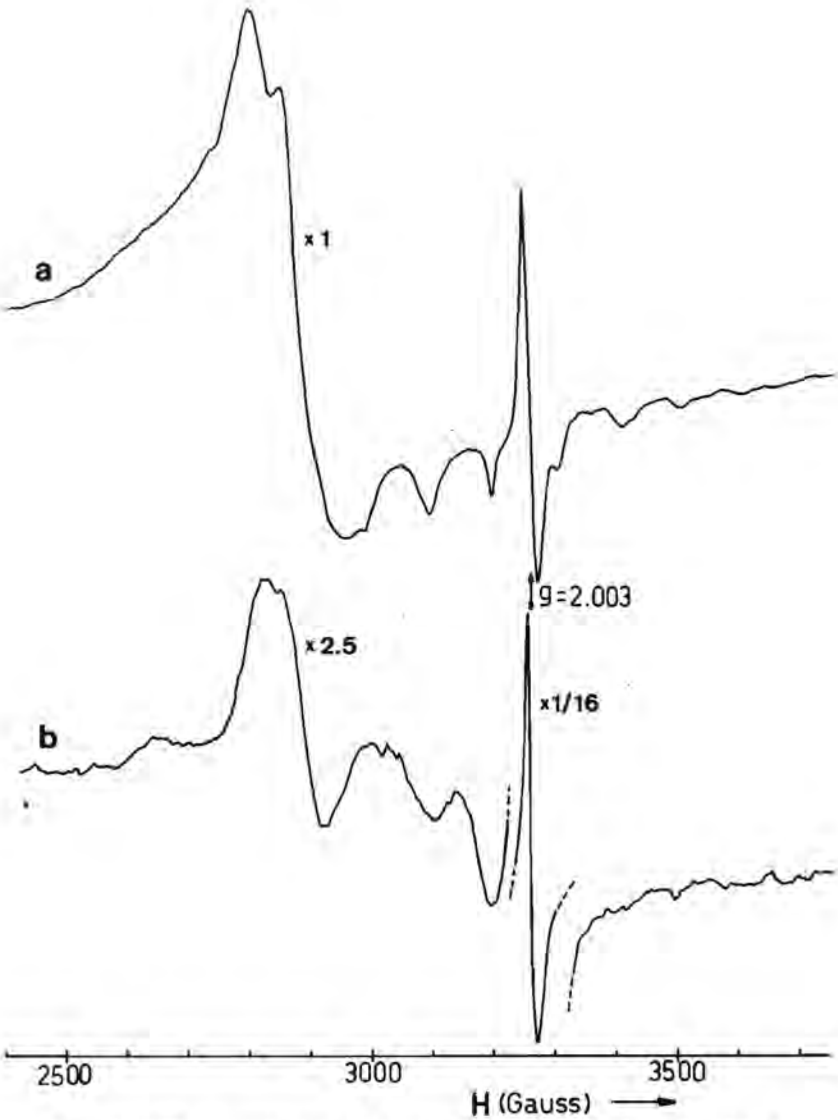

Fig. 3. a) ESR spectrum of polymer attached CoPc$(NH_2)_4$ suspended in DMF, degassed under vacuum. Recorded at -140°C.
Spectrometer settings: microwave frequency 9.11 GHz, power 50 mW, modulation amplitude 4 Gauss, receiver gain 8×10^2.
b) Spectrum after exposure to NH_3 gas of 1 atm. pressure and subsequent aeration. Recorded at -140°C after standing overnight at room temperature. Spectrometer settings: same as sub a) except receiver gain 2×10^3, resp. 5×10^1 for the $g = 2.003$ signal.

upon swelling of the catalyst in water, an increase of signal intensity of mononuclear cobalt centres is observed (factor ~ 4). This can be understood by considering that swelling involves expansion of the polymeric chains, giving rise to a further elimination of site-site interactions, and thus producing a higher number of mononuclear cobalt sites. One can roughly estimate from signal intensity measurements carried out on the catalyst suspended in water, that its fraction of isolated mononuclear sites amounts to about 30%. This result is quite remarkable taking into account the inherent tendency of metal phthalocyanines to dimerize in aqueous media [6, 7].

However, to account for the higher activity of the polymer bound catalyst, mononuclear sites have to be retained under catalytic conditions. Only in that case, catalytic operation would proceed through the very reactive mononuclear superoxo-adducts (I) instead of the less reactive dimers (II), normally encountered in a homogeneous solution. Therefore, we examined the ability of the polymer matrix to prevent such a transformation into (II). A ready opportunity to test this ability of the matrix is offered when relatively large amounts of NH_3 are added to the polymeric catalyst. As we found earlier [5], exposure of a homogeneous CoPc solution in DMF to NH_3 gas of 1 atmosphere pressure and subsequent aeration gave rise to disappearance of the ESR signal within about 1 minute, due to formation of the diamagnetic dimer (II). On the other hand, the polymer bound catalyst suspended in DMF reacts quite differently; the same treatment in this case initially does not result in any observable loss of signal. Only after standing overnight at room temperature a fall in intensity (~ factor 5) of the cobalt signal is observed (Fig. 3). It may be expected that the observed selective suppression of the dimerization step within the reaction network, will give rise to an appreciable contribution of reactive mononuclear oxygen adducts in the catalytic reaction.

The effective site isolation as observed here, seems to be in contradiction with the lack of rigidity found for even highly cross-linked polymers [8]. However, apart from rigidity other factors may play a decisive role in the ultimate result obtained. For instance, our system is characterized by a *low local concentration* of polymer attached Co-phthalocyanines, which are rather *bulky* planar systems, *covalently bonded* through their ringsubstituents onto the polymeric carrier. The latter two characteristics will impose serious restrictions towards mobility of the attached catalyst.

The effect of the local concentration upon interaction between polymer bound groups may best be illustrated by results reported by Fuhrhop *et al.* [9]. With the aim to create 5-coordinate Fe-porphyrin complexes these authors used polymer bound imidazole ligands. In the case of a *high concentration* of attached imidazole groups, however, it appeared that the polymer matrix was not sufficiently rigid to prevent 6-coordination. A similar result was reported by Collman *et al.* [10]. On the other hand, use of polymers with a significantly *reduced imidazole content* led almost completely to the formation of the desirable 5-coordinate complex [9]. Hence, under these circumstances the polymer matrix did effectively prevent interaction between polymer bound groups.

Fuhrhop [9] demonstrated that the 5-coordinate Fe(II)-porphyrin, present in low local concentration, proved to be an excellent reversible oxygen carrier *at room temperature*. Obviously, the formation of dioxygen bridged dimers between these bulky groups is inhibited under these conditions. Comparable results are reported by other workers [1, 11]. These observations combined with our own results suggest that polymer attachment may provide an excellent tool to prevent unfavourable dimerization reactions. However, additional factors such as the use of bulky groups in a low local concentration and a tight anchoring to the matrix, have to be satisfied.

A small signal observable at $g \sim 2.003$ (Fig. 1) deserves special comment. This featureless signal of narrow linewidth (~ 15G), absent in the carrier, was present in all polymer attached cobalt phthalocyanines prepared in our laboratory. Usually, its intensity is relatively low, but under conditions that favour the formation of the binuclear oxygen adduct (II) as described before (*i.e.* in the presence of excess of NH_3 and of oxygen) a sharp rise in intensity occurred (factor ~ 15; *see* Fig. 3). A similar signal was already observed by us during the conversion of a *homogeneous* CoPc solution into the binuclear oxygen adduct [5]. Consistent with results reported by Lever *et al.* [12], this signal was assigned to a $Co(III)Pc^{++}.O_2^{--}$ radical generated by oxidation of the Pc-ring. Elimination of this radical species then will take place in the subsequent coupling reaction with CoPc leading to (II). But in the case of the polymeric catalyst this coupling reaction is strongly inhibited. As a consequence, the intensity of the $g \sim 2.003$ signal should be higher in the polymeric catalyst than in its homogeneous counterpart. This prediction could be confirmed by our experimental data.

Very recently, further support for our assignment of the $g \sim 2.003$ signal was obtained from investigations reported by Raynor *et al.* [13] on the origin of the ESR signal in solid diamagnetic phthalocyanines. They concluded that the observed sharp signal at $g \sim 2.003$ arises from a charge-transfer interaction between the phthalocyanine and coordinated dioxygen under formation of a Pc^+ radical cation and a reduced dioxygen ligand.

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CHAPTER 4

AUTOXIDATION OF MERCAPTANS PROMOTED BY A BIFUNCTIONAL CATALYST

Summary

A new bifunctional catalyst of Cobalt-Phthalocyanine (CoPc) has been developed in which an efficient co-operation between oxidation catalyst and basic sites has been attained. Investigation of this bifunctional catalyst has led to the following interesting observations: 1. A significant enhancement in specific activity is observed for the bifunctional system compared with the corresponding NaOH/CoPc-system (factor 50); the polymeric character of the base appears to be essential. 2. The amount of basic groups incorporated in the polymer, necessary for getting this high activity, is less than the amount of NaOH used in the corresponding NaOH/CoPc-system by about a factor of 100 à 1000. From the reaction products, being disulfide and H_2O_2, the accumulated H_2O_2 is probably responsible for the formation of traces of sulfuracids, which may occupy and thus deactivate the basic sites of the polymer in subsequent runs. The high activity of the bifunctional catalyst may be ascribed to a fundamental change in the mechanism of oxidation, which also can be inferred from the notably reduced value of the apparent activation energy observed for the bifunctional catalyst compared with its NaOH/CoPc-counterpart (8 resp. 12.7 kcal/Mole).

1. Introduction

Multifunctionality seems to be one of the main characteristics of enzymes. This presumably is connected with their high activity and selectivity. Model systems can be useful to elucidate the factors governing the cooperative interaction between various catalytic sites. Polymers generally have been used in the preparation of model systems, since they offer an opportunity to introduce a variety of chemical modifications.

For hydrolysis reactions remarkable results were already obtained, using multifunctional polymers - incorporating imidazole groups - as catalyst *(1, 2)*. Very reactive oxidation catalysts can be obtained by complex formation *(3)* of modified polymers with metal ions *(4-6)*.

The purpose of this work is to synthesize bifunctional catalysts composed of Cobalt-Phthalocyanine (CoPc) and a variety of polymeric bases, the catalyst obtained being tested for the oxidation of mercaptan in aqueous media. Earlier experiments in this laboratory *(7)* have shown polymer attached CoPc to be much more active than their homogeneous counterpart, however, the presence of additional base (NaOH) appeared to be necessary.

Other experiments carried out in organic media by Rollmann *(8)* point to the possibility of cooperation between polymeric base and CoPc.

2. Experimental

2.1 Supporting materials

- Poly(ethylene imine): PEI

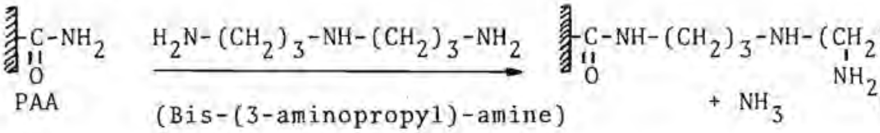
Polymin P (50% Sol. in H_2O), N = 16% by wt; Fluka
Cross-linked PEI: glutardialdehyde used as agent. Product washed with cold water and Soxhlet-extraction (designated PEI-X)

- Poly(vinylamine): PVAm

Prepared according to method given by Bloys van Treslong *(9)*.
Anal. PVAm.HCl: C/N-ratio = 2.03, N/Cl-ratio = 1.02.
Desalting of PVAm.HCl by use of DOWEX 2 (Fluka).

- Poly(acrylamide) modified by amine groups: PAA-NH_2

Poly(acrylamide) (= PAA) obtained by polymerization of acrylamide (recryst. from chloroform) in ethanol as solvent; initiator AIBN, T = 63°C, N_2-atmosphere.
Yield 98%; $[\eta] = 0.3355 \sim M_v = 30.000$ *(10)*.
Introduction of amine groups according to Inman and Dintzis *(11)* (equation 1).



$$\underset{\text{PAA}}{-\underset{\underset{O}{\|}}{C}-NH_2} \xrightarrow[\text{(Bis-(3-aminopropyl)-amine)}]{H_2N-(CH_2)_3-NH-(CH_2)_3-NH_2} -\underset{\underset{O}{\|}}{C}-NH-(CH_2)_3-NH-\underset{\underset{NH_2}{|}}{(CH_2)_3} + NH_3 \qquad (1)$$

- Silica modified by amine groups: Silica-NH_2

Silica: Davison Grade 950 (Koch-Light); sieve fraction 0.125 mm < d < 0.16 mm, pore volume 0.4 ml/g, spec. surf. area 500 m^2/g.
Dried and coupled with γ-amino-propyl-triethoxy-silan according to Horner and Schumacher *(12)*.

2.2 Analysis of base content (Table 1)

The soluble polymers (PEI and PAA-NH_2) were titrated with 0.1N HCl. Titration of PAA-NH_2 shows the successive neutralization of primary amines (pKa = 9.6) and sec. amines (pKa = 7.2), ratio 1/1 according to product formation as given in eq. (1).
The base content of PVAm was calculated from the nitrogen-content of the corresponding PVAm.HCl (N = 15.2%).
The insoluble supports were analyzed according to the method usually applied to weak-base ion exchangers.

TABLE 1

Resulting basic carriers

Material	Base μ-equiv./mg
PEI	17.3
PEI-X	17.2
PVAm	18.0
PAA-NH_2(1)	2.54
PAA-NH_2(2)	1.58
Silica-NH_2	0.40

2.3 Cobalt (II) 4, 4', 4'', 4'''-tetrasulfo-phthalocyanine: CoTSPc

Prepared according to Weber and Busch *(13)*; recryst. by cooling an aqueous sol. and addition of ethanol. The precipitate was washed with ethanol and refluxed during 4 hrs in abs. ethanol, product dried in vacuo over P_2O_5; yield 75%.
Anal.: $C_{32}H_{12}N_8O_{12}S_4Na_4Co.7H_2O$ calcd.: C = 34.75, H = 2.17, N = 10.13, Na = 8.33, Co = 5.34. Found C ; 34.68, H = 2.06, N = 10.31, Na = 8.1, Co = 5.1%.

2.4 Catalyst preparation

Method 1: A CoTSPc-solution in methanol was added to the carrier, causing decolorization of the solution. The carrier/ CoTSPc-complex was washed with methanol and dried in vacuo.

Method 2: "In situ" preparation of the polymeric catalyst *i.e.* polymer as well as CoTSPc were added separately to the reaction liquid.

No substantial differences in activity were noticed between the products of the two. Only the silica-system was prepared according to method 1.

2.5 Oxidation conditions

The oxidation was carried out in an all-glass Warburg apparatus provided with a magnetic stirring device. The temperature of the reaction liquid was maintained constant by a thermostating jacket. The rate of oxidation was determined by measuring the amount of oxygen consumed (ml/min.) at constant oxygen pressure ("initial rate" was calculated for consumption of first 20 ml of oxygen). A representative experiment was carried out in 130 ml H_2O oxidizing 1 ml (= 14.25 mmol) of mercapto-ethanol (ME) with vigorous stirring; $P(O_2) = 1$ atm., $T = 24\,^{\circ}C$. The amount of catalyst was chosen in such a way that an appropriate rate of oxygen consumption resulted (0.5 - 5 ml/min.).

H_2O_2 was quantitatively analyzed at the end of the oxidation according to a spectro-photometric method using $TiCl_3$-H_2O_2 as reagent *(14)*.

2.6 Oxidation reaction

The oxidation of mercaptan (RSH) resulted in the formation of disulfide (RSSR) together with a non-stoichiometric amount of H_2O_2. The overall reaction can be represented by (4) being a combination of (2) and (3).

$$\begin{array}{llllr}
4RSH + O_2 & \longrightarrow & 2RSSR + 2H_2O & x(1-a) & (2) \\
4RSH + 2O_2 & \longrightarrow & 2RSSR + 2H_2O_2 & x(a) & (3) \\
\hline
4RSH + (1+a)O_2 & \longrightarrow & 2RSSR + 2(1-a)H_2O + 2aH_2O_2 & & (4)
\end{array}$$

3. Results

It is well established *(15)* that the catalytic autoxidation of mercaptans (RSH) is appreciably accelerated by addition of a base, such as alkaline hydroxide, the thiolate anion (RS^-) being the species susceptible to reaction with oxygen.

TABLE 2

Maximal rates observed

System	Basic agent	Base μ-equiv.	CoTSPc nanomoles	v-specific ml/min. μ-mole
homogeneous non-polymeric	-	-	200	4
	NaOH	6000	200	22
	BAA[a]	60	10	23
homogeneous polymeric	PAA-NH_2(2)	163	10	740
	PEI	35	10	235
	PVAm	100	5	930
non-soluble supports	Silica-NH_2	53.6	50	52
	Imac-A27[b]	640	10	55
	PEI-X	76	10	31

[a] BAA = Bis-(aminopropyl)-amine

[b] Imac-A27: A weak base ion-exchanger with epoxy amine matrix (AKZO)

$$2RSH + 2OH^- \longrightarrow 2RS^- + 2H_2O \qquad (5)$$

$$2RS^- + 2H_2O + O_2 \xrightarrow{catalyst} RSSR + H_2O_2 + 2OH^- \qquad (6)$$

An ideal catalyst therefore should be bifunctional *i.e.* possess oxidation sites and basic sites in cooperative interaction. Therefore it was tried to bind Cobalt-Phthalocyanine covalently onto a carrier which contains basic groups. This led us to the observation that also *without* covalent bonding a very reactive catalyst system was obtainable.

Adding a polymeric base, or an inorganic carrier modified with amine groups, was sufficient to improve the catalytic activity of an aqueous solution of CoTSPc. Soluble polymers are particularly effective in raising the reaction rate *(Table 2)*. It is noteworthy that a significant enhancement in specific rate was observed with very low amounts of basic groups, amounts that were a factor of 100 less than required in the NaOH/CoTSPc-system. Moreover, the low value found for the specific rate when using a non-polymeric amine, *i.e.* bis-

TABLE 3

Influence of basic groups on specific activity (10 nanomoles of CoTSPc applied)

Nr.	Support[a]	Basic groups μ-equiv.	NaOH μ-equiv.	v-specific ml/min.μ-mole
1	PAA-NH_2(1)	10.8	-	165
2	PAA-NH_2.HCl[b]	-	-	10
3	PAA	-	-	4
4	-	-	-	5
5	PAA-NH_2(1)	10.8	6000	25
6	-	-	6000	22

[a] If applied here: 4.25 mg

[b] A stoichiometric amount of HCl (11 μ-equiv.) added.

(amino propyl)-amine (BAA), shows that the polymeric character of the base is essential for obtaining high activities.

3.1 Influence of additional base or acid

To evaluate the role of the amine groups of the polymers a stoichiometric amount of HCl was added to the system sufficient to neutralize the amine groups, alternatively, poly-(acrylamide) *without* incorporated basic groups was used. From the results given in *Table 3* the essential role of the amine groups becomes evident.

On the other hand, addition of the normal amount of NaOH results in significant loss of activity. Actually, a comparison of the results of exp. 5 and 6 shows the polymeric base in this case does not contribute to the activity. In this context the observation, that addition of a NaOH-solution to a preformed polymer/CoTSPc-complex resulted in decoloration of the polymer, is of significance. The bond of CoTSPc with the polymer apparently was broken by the addition of NaOH.

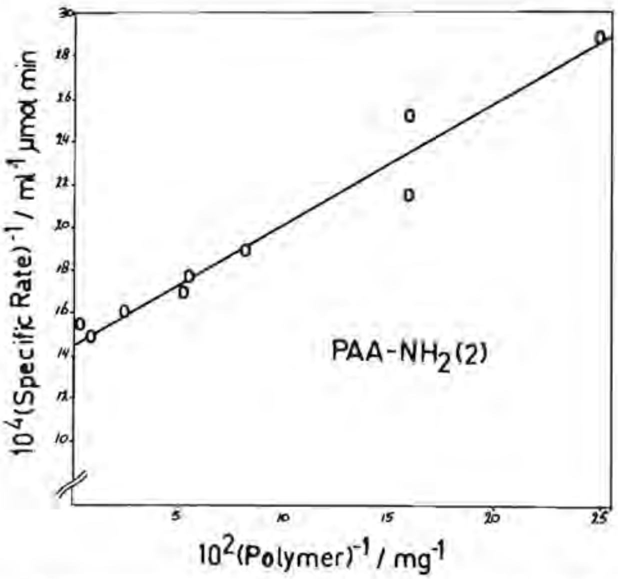


Fig. 1. Lineweaver-Burk plot of specific rate of oxidation versus the amount of polymer (applied PAA-NH$_2$(2), 10 nanomoles CoTSPc).

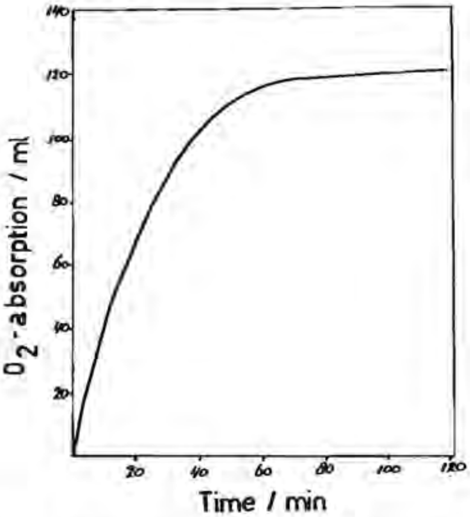


Fig. 2. Oxygen absorption during a catalytic run (20 nanomoles of CoTSPc, 4.26 mg PAA-NH$_2$(1), 1ml ME, 130 ml H_2O; $P(O_2)$ = 1 atm., T = 23°C).

TABLE 4

Variation of the amount of bifunctional catalyst (applied: PAA-NH_2(1))

Basic groups µ-equiv.	CoTSPc nanomoles	$\frac{\text{base}}{\text{CoTSPc}} \times 10^{-3}$	v-specific ml/min.µ-mole
10.8	10	1	155
21.6	20	1	223
10.7	5	2	144
21.3	10	2	261
21.6	5	4	200
42.8	10	4	306

3.2 Kinetic measurements

The rate as function of the amount of polymeric base (PAA-NH_2) increases up to a maximal value. A Michaelis-Menten description of the kinetics fits rather well as can be inferred from the Lineweaver-Burk plot *(fig. 1)*. The base/CoTSPc-ratio seems not to be a very important factor, rather the amount of polymeric base dictates the specific activity of the catalytic system *(Table 4)*.

3.3 Stability of the catalytic system

During the catalytic oxidation, using PAA-NH_2 or Silica-NH_2 as basic material, a significant amount of H_2O_2 is formed, giving rise to increase of the volume of oxygen, required for total conversion of 1 ml of ME. A typical plot of oxygen absorption versus time is shown in *fig. 2*.

After finishing the oxygen absorption, measurement of the amount of H_2O_2 and the total oxygen absorption allows the fractional conversion of RSH into RSSR to be calculated. From the values in *Table 5* it is clear that complete conversion has not been obtained in all cases. Apparently, the catalyst becomes gradually deactivated during the course of the reaction. How-

TABLE 5
H_2O_2-accumulation (PAA-NH_2(1): 4.2 mg ~ 10.7 μ-equiv. of base;
Silica-NH_2: 136 mg ~ 53.9 μ-equiv. of base)

Nr.	Base	CoTSPc nano-moles	Rate ml/min.	V_{O_2} (total) ml	$N_{H_2O_2}$ mmoles	η[a]
1	PAA-NH_2(1)	20	3.4	119	2.52	0.99
2	PAA-NH_2(1)	40	4.5	128	3.44	0.95
3	PAA-NH_2(1)	80	6.1	128	3.62	0.93
4	PAA-NH_2(1)	160	3.7	115	3.30	0.82
5	Silica-NH_2	50	2.0	116	2.15	0.99

[a] η = fractional conversion of RSH into RSSR

TABLE 6
Activity in successive runs[a]
(PAA-NH_2(1): 8.5 mg ~ 21.5 μ-equiv. base;
Silica-NH_2: 135.8 mg ~ 53.9 μ-equiv. base)

Nr.	Base	CoTSPc	V_{O_2} (total) ml	Rate ml/min	η[b]
1	PAA-NH_2(1)	33	120	7.4	0.85
1a			85	3.3	
1b			-[c]	0.1	
2	Silica-NH_2	50	116	2.0	0.99
2a			84	1.6	
2b			81	1.5	
2c[d]			22	0.2	

[a] At the end of each run a subsequent 1 ml-portion of mercapto ethanol was added.

[b] η = fractional conversion, determined after the absorption of oxygen stopped.

[c] not measured.

[d] measured after storing overnight

TABLE 7
Stability of the catalyst

Nr.	Silica-NH_2 mg	Silica-NH_2 μ-equiv.	CoTSPc nanomoles	rate ml/min
1	135.7	53.9	50	1.8
1a				1.1[a]
1b				0.8[a]
1c				0.7[a]

[a] After 15 min. of reaction time for the previous run, the activated silica was separated from the liquid, washed with double dest. H_2O, and reused in a freshly prepared H_2O/ME-solution.

ever, it is possible to recover catalytic activity, at least in part, by adding an additional 1 ml-portion of ME *(Table 6)*. Repetition of this cycle, however, gives rise to a decrease in initial rate, particularly if the previous reaction mixture has been stored overnight (exp. 2c).

Catalytic systems using heterogeneous bases allow an alternative way of determining their stability, namely by separation of the heterogeneous base from the reaction liquid and reuse of it in a fresh aqueous solution of ME (1 ml), without further addition of CoTSPc. By doing so, only the fractional amount of CoTSPc fixed to the matrix will be regained. From measurement of the activity of the next run an estimate can be made of this fraction of CoTSPc situated on the carrier during the catalytic oxidation. From the results of *Table 7*, combined with those found in *Table 6*, it can be calculated that about 75% of the total amount of CoTSPc, present in the first run, will remain fixed onto the silica surface during the reaction.

4. Discussion

4.1 Bifunctionality

From the results obtained it can be concluded that a *bifunctional* catalyst can be created by combining a polymeric base with Cobalt-Tetrasulfo-phthalocyanine (CoTSPc). Investigation of this catalyst in the autoxidation process of mercapto-ethanol has led to the following remarkable observations:

1. A significant enhancement in specific activity is observed for the bifunctional system compared with the conventional NaOH/CoTSPc-system (factor 50).
2. The amount of basic groups incorporated in the polymer, required for such a high activity, is less than the amount of NaOH used in the corresponding NaOH/CoTSPc-system by about a factor of 100 to 1000.
3. Soluble polymers give rise to the most active systems, but also microgels or solid carriers can be used as for instance cross-linked polymeric bases or inorganic materials, such as silica modified with aminogroups.
4. The polymeric bases are much more effective in raising the activity of the catalytic system than their monomeric counterpart.
5. The catalytic system obeys Michaelis-Menten kinetics with respect to the amount of polymeric base.

The Michaelis-Menten kinetics observed indicates the formation of a complex between the polymeric base and CoTSPc, in equilibrium with its free components, while this complex acts as the actual catalyst. A particularly effective cooperation between CoTSPc and the polymeric basic groups has to be assumed within such a complex, considering the high catalytic activity using relatively low amounts of polymeric base.

4.2 Characterization of the catalytically active complex

In order to elucidate the mode of binding in the catalytic complex, we should ascertain the influence of the thiol (RSH) in modifying the basic carrier.

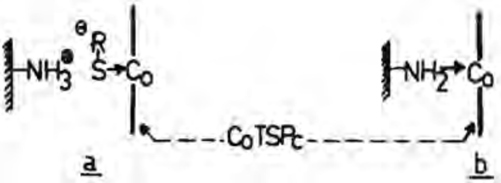


Fig. 3. Representation of the Polymer/CoTSPc-complex
a: during the catalytic oxidation
b: in the absence of thiol

$$-NH_2 + RSH \rightleftharpoons -NH_3^{\oplus}\ {}^{\ominus}SR \qquad (7)$$

Under reaction conditions, using 0.1M ME ($pK_a = 9.6$), the aqueous solution will be slightly acidic (pH ~ 5.3). Under these circumstances equilibrium (7) will be strongly shifted to the right: the approximate ratio of RNH_2/RNH_3^+ ($pK_a = 9.6$) then will be $10^{-4.3}$. Hence the amount of non-protonated amine can be neglected.

Complex formation between CoTSPc and the modified carrier most probably will occur by a coordinative interaction between the matrix-bound mercaptide anions and the Cobalt nucleus of CoTSPc as shown in *fig. 3a*. Similar, non-polymeric, mercaptide complexes of Fe(II)-Porphyrins have been shown to exist and were studied as a model for Cytochrome P-450 *(16)*. From these studies it became apparent that the sulfur in the mercaptide anion is a strong π-electron donor, giving rise to the high affinity for oxygen as exhibited by these complexes.

It should be noted here that a complex between CoTSPc and the amine carrier could also be obtained in the absence of RSH using methanol as the solvent for CoTSPc (*see 2.3*). In this case complex formation can be accomplished by a coordinative bond between the non-protonated amine groups and the Cobalt nucleus *(fig. 3b)*.
Such a mode of interaction seems to be conceivable, considering the high affinity of low molecular N-bases for the central metal atom, due to their strong σ-donor properties, as ob-

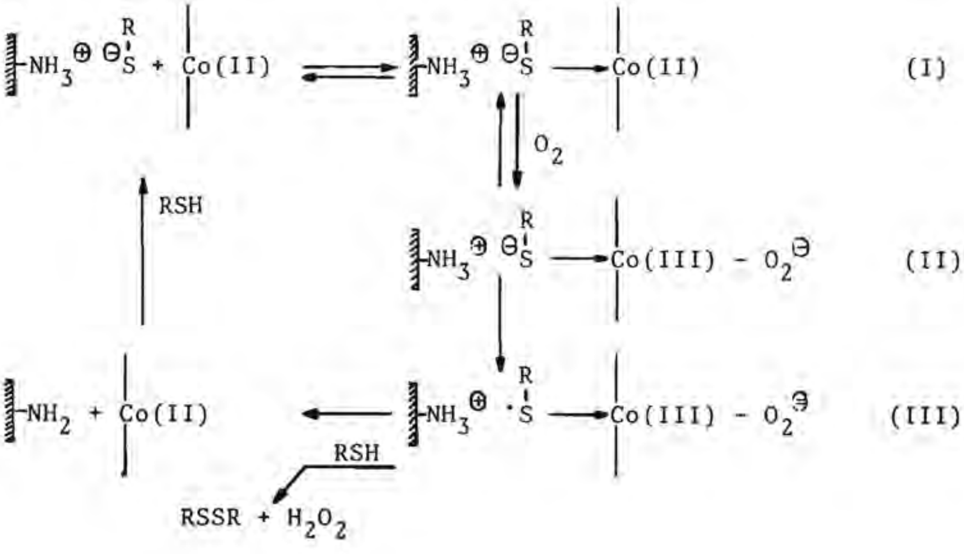
served earlier for analogous planar metal complexes *(17, 18)*. As stated before, such a direct N/Co-interaction does not seem to be very likely under catalytic conditions.

4.3 Mechanistic interpretation

Optical measurements carried out by us during the oxidation of RSH in the NaOH/CoTSPc-system give evidence for the existence of an intermediate binuclear dioxygen adduct. Presumably this is formed from oxygenation and subsequent dimerization, the dioxygen adduct being the main species present during this particular reaction *(19)*.

For the matrix-bound CoTSPc an analogous oxygenation reaction may be expected. However, the dimerization step may be partially or completely inhibited as a result of binding the CoTSPc to a polymer or inorganic carrier, as *e.g.* silica. These considerations have led to a suggested reaction sequence as given in *Scheme 1*.

Scheme 1



The internal electron transfer in (II) from coordinated RS^- to O_2^- resulting in (III) seems to be a very attractive one because formation of the peroxo-complex will be thermodynamically strongly favored over the superoxo-complex as can be inferred from the high standard potential for the reaction $HO_2^{\cdot} + H^+ + e^+ = H_2O_2$ ($E^o = 1.17V$ *(20)*) combined with the low value of the $RS^{\cdot}/RS^-$ couple being $E^o \sim -0.3V$ *(21)*. The subsequent reaction with another molecule of RSH may then give rise to product formation (RSSR and H_2O_2).

Although the proposed mechanism is a tentative one demanding further experimental evidence, the crucial point in this mechanism leading to a strongly enhanced reaction rate should be the separation of the catalytic units from each other, *thus avoiding dimerization reactions*, normally occurring in the NaOH/CoTSPc-system.

In the following, two major effects of the presence of a polymer carrier will be discussed, viz. (1) shielding and (2) diffusion controlled dimerization.

(1) *Shielding*: In the relevant, very diluted, solutions (*e.g.* 4 mg polymer per 130 ml H_2O) in a good solvent, the polymer molecules will be present as separate, relatively extended coils, which certainly do not fill all the space. Under the above conditions it then can be calculated for a typical experiment (nr. 1 in *Table 3*), that the number of coils per Co-unit amounts to about 15, which means that in first approximation there are no *coils containing more than one CoTSPc unit*. As it may be expected that the polymer bound RS^- coordinatively interact with the Co-nucleus in CoTSPc, the catalyst will preferably be surrounded by polymer segments. The latter shielding effect will be enhanced by the high local concentration of coordinative sites within the polymeric coil, due to the non-homogeneous features of dilute polymer solutions. As a result, the CoTSPc will be shielded, by the polymeric environment, against dimerization reactions, which readily occur without the use of specifically interacting polymers.

(2) *Diffusion controlled dimerization*: Dimerization of polymer bound CoTSPc involves the reaction of two large poly-

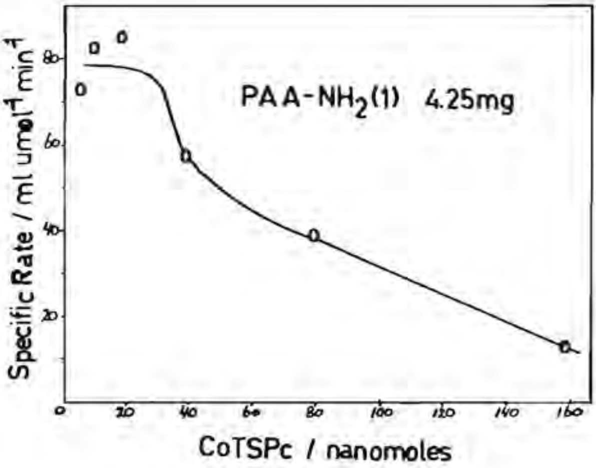


Fig. 4. Relationship between specific rate and the amount of CoTSPc (polymer applied: PAA-NH_2(1); 4.25 mg ~ 10.8μ-equiv. base).

meric species, while the competing reaction only involves electron transfer within the complex. A reasonable estimation of the upper limit of the apparent rate constant of this dimerization reaction seems to be the rate constant of the (diffusion controlled) termination in radical polymerizations, *i.e.* 10^7 $M^{-1}.sec^{-1}$. Since the dimerization in NaOH/CoTSPc-systems appears to be an intrinsically fast reaction (approx. order of 10^9), it becomes evident that the dimerization of polymer bound CoTSPc will be diffusion controlled to such an extent as to favor the competing, fast electron fransfer reaction.

Further supporting evidence for such a fundamental change in the mechanism of oxidation in the presence of specific polymers has been obtained by measurements of the observed overall activation energy, being 7.8 kcal/mole for the PAA-NH_2/CoTSPc-system and 12.7 kcal/mole for the NaOH/CoTSPc-system. For the *heterogeneous* silica-NH_2/CoTSPc-system even a lower value of 3.4 kcal/mole was obtained, however, this may be attributed to substrate limitation due to diffusion within the narrow pores of the matrix ($\bar{d}$ = 32 Å).

It may be expected that above a certain concentration of CoTSPc, dimerization reactions of the catalyst can no longer be avoided by the polymer coil segments.

A study of the specific activity as a function of the amount of CoTSPc, bound to the polymer will serve to shed light on this question. *Fig. 4* shows the specific activity to be independent of the total amount of CoTSPc, if used at low concentration. At higher concentration levels, however, the specific activity diminishes with further addition of CoTSPc, which is ascribed to dimerization processes, now becoming operative. One should note that at too high CoTSPc-level even a decrease in *absolute* rate can be effected by an additional amount of CoTSPc.

The proposed equilibrium between free CoTSPc and CoTSPc bound to the matrix (*Scheme 1*) can account for the deactivation of the catalyst on addition of NaOH or HCl. Since additional NaOH generates free RS^--species in the solution, which will compete with the polymer-bound RS^- for CoTSPc ligation, the catalyst will move away out of the polymeric environment. On the other hand, a strong acid will occupy the amine groups, thus preventing the thiolate groups from coordinating to the polymeric base.

The latter phenomenon may also be the reason for the loss in activity observed in subsequent runs: by the action of the accumulated H_2O_2 traces of sulfur-acids may be generated *(22)* poisoning the catalyst. An additional amount of RSH initially will be able to partly drive out these strong acidic species, but as the accumulation of strong acids will grow this recovery of active sites will diminish.

The bifunctional catalyst is now under continued investigation in order to elucidate the details of binding of the complexes and the mechanism of oxidation. Improvement of the stability of the catalyst during the oxidation, as well as during regeneration with alkaline solutions, will be pursued by means of fixation of the catalyst to the carrier by a covalent bond.

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CHAPTER 5

INVESTIGATION OF BIFUNCTIONAL CATALYSTS WITH IMPROVED STABILITY

Summary

An effective catalyst for the autoxidation of mercaptans should possess oxidation sites and basic sites in cooperative interaction. Such a bifunctional catalyst was prepared using poly(vinylamine), that acts both as supplier of basic sites and as a carrier for the oxidation catalyst cobalt(II)-4, 4', 4'', 4'''-tetracarboxy-phthalocyanine. Polymer attachment of the cobalt-phthalocyanine was achieved by complexation through polymeric amine groups (catalyst I), as well as by formation of a peptide linkage between the phthalocyanine ring system and the polymeric carrier (catalyst II). Both methods of coupling provided bifunctional catalysts, not requiring additional base, with extremely high activities.

The presence of low amounts of alkaline base did not influence the initial activity appreciably, but it had a positive influence on the stability of the catalysts by allowing *in situ* neutralization of acidic by-products. However, addition of higher amounts of alkaline base resulted in a loss of activity ascribed to a reduction of the local substrate concentration. In case of catalyst I this loss of activity is more pronounced, due to rupture of the polymer/cobalt-phthalocyanine complex.

It was demonstrated that the polymeric catalysts can also be applied in toluene, provided that small amounts of water are present. Most probably water plays an important role in the proton transfer, which is an essential feature of the autoxidation process.

1. Introduction

It is well established [1], that the catalytic autoxidation of mercaptans (RSH) is appreciably accelerated by addition of a base, the generated thiolate anion (RS^-) being the species susceptible to reaction with oxygen.

$$2RSH + 2OH^- \longrightarrow 2RS^- + 2H_2O \qquad (1)$$

$$2RS^- + 2H_2O + O_2 \xrightarrow{\text{catalyst}} RSSR + H_2O_2 + 2OH^- \qquad (2)$$

Metal ions [2, 3] and metal complexes [4, 5] can be used as catalysts in this oxidation. A class of highly active catalysts is formed by transition metal phthalocyanine compounds [6]. Because of this high activity, metal phthalocyanines have also industrial application as catalysts in sweetening processes [7, 8]. The required base - as a rule alkaline hydroxides are used - is usually added separately to the reaction medium.

Recently [9] we showed, that a particularly active catalytic system could be obtained using a polymeric base - instead of alkaline hydroxide - in combination with cobalt(II) 4, 4', 4'', 4'''-tetrasulfo-phthalocyanine ($CoPc(SO_3Na)_4$) as oxidation site. We could conclude from the experimental results that this bifunctional catalytic system consisted of a complex between the polymeric carrier and the cobalt-phthalocyanine (CoPc).

While the activity of this bifunctional catalyst in aqueous media was appreciably higher than the activity of the conventional CoPc/NaOH system (about a factor 100), a disadvantage of the polymeric system was the loss of activity observed in successive runs. This deactivation was ascribed to strong sulfur containing oxo-acids, generated in traces during the reaction, which poison the basic groups of the polymer. It was expected that this poisoning could be avoided by employment of small amounts of alkaline hydroxide in order to neutralize these strong acids. However, when adding NaOH to the polymeric catalyst we found a dramatic deactivation, due to rupture of the polymer/$CoPc(SO_3Na)_4$

complex.

Based on these observations we started an attempt to prepare a catalyst with *enhanced stability* in the presence of small amounts of NaOH. This would allow *in situ* removal of sulfur acids, while avoiding concurrent decomposition of the polymer/CoPc complex. Improvement of the catalyst was attempted along two routes. Firstly, poly(vinylamine) was used as the polymeric amine carrier, having stronger complexing abilities than the polymer previously used, *i.e.* poly(acrylamide) with incorporated amine groups. A further improvement was aimed at linking the CoPc to the polymer via a *covalent* bond between the phthalocyanine ring substituents and the amine groups of the polymeric carrier. For instance a peptide linkage can be formed by using the tetracarboxy substituted cobalt-phthalocyanine ($CoPc(COOH)_4$). The effect of these modifications on the stability of the resulting catalysts in aqueous media is reported in this paper.

A further aim of this study was to examine to which extent these catalysts can be employed in apolar media. The results may shed light on the role of water in the catalytic mechanism, while it would be of technological interest if the bifunctional catalyst could also be used in the absence of water. For example this would offer the opportunity of a more simple removal of mercaptan sulfur compounds from cracked gasolines (sweetening), avoiding the usually applied two-phase process.

2. Experimental

Poly(vinylamine-hydrochloride) (PVAm-HCl)

PVAm-HCl was obtained from poly(tert-butylvinylcarbamate), PtBVC, by hydrolysis in 10N hydrochloric acid/ethanol solution (1:1, v/v) [10]. PtBVC was prepared from the corresponding monomer under nitrogen in benzene with azoisobutyronitrile, AIBN, as initiator (reaction time: 48 hrs, T = 60°C). PtBVC with different average molecular weights were obtained by varying the amount of AIBN. Number average molecular weights -

from viscosity measurements in toluene at 25°C, calculated with data of Bloys van Treslong [10] - were in the range $3.8 \cdot 10^4 \leqslant \bar{M}_n \leqslant 14.4 \cdot 10^4$.
Anal. PVAm-HCl.xH_2O (24 hrs. dried at 30°C and 1 mm Hg). Found: C 28.14, H 7.71, N 16.40; C/N (atomic ratio) 2.00. Calcd. for PVAm-HCl.0.3H_2O: C 28.28, H 7.83, N 16.50; C/N (atomic ratio) 2.00.
Hughes *et al.* [11] report PVAm-HCl.0.5H_2O as product. The IR-spectrum of PVAm-HCl is in accordance with the data in the literature [11, 12].

Poly(vinylamine) (PVAm)

An aqueous solution (2-3%) of PVAm-HCl was passed through an ion-exchange column (Amberlite IRA 410 in OH^- form), thereafter the column was rinsed with water. The effluent collected from the column was concentrated to about 5% under reduced pressure; PVAm could be obtained by precipitation of the resultant solution in acetone p.a [12]. All PVAm-solutions were kept continuously under nitrogen to prevent absorption of carbon dioxide. Calculated molecular weights - from viscosity measurements in water with 0,01 M NaOH and 0,1 M NaCl at 25°C - were in the range $1.5 \cdot 10^4 \leqslant \bar{M}_n \leqslant 6 \cdot 10^4$. The IR-spectrum of PVAm is in accordance with the data in the literature [12].

Cobalt(II) 4, 4', 4'', 4'''-tetracarboxy-phthalocyanine ($CoPc(COOH)_4$)

Prepared with trimellitic acid (1, 2, 4-tricarboxybenzene) as starting-material on the analogy of the method given by Weber and Busch [13]. The crude reaction product was purified by dissolving it in 0,1 N NaOH and subsequent precipitation in ethanol p.a. The precipitate was isolated with the aid of a centrifuge and washed four times with ethanol p.a. The obtained product is (somewhat impure) cobalt(II) 4, 4', 4'', 4'''-tetraamide-phthalocyanine ($CoPc(CONH_2)_4$).
Anal. Found: C 55.56, N 20.73, Co 7.4; atomic ratios: C/N = 3.13, N/Co = 11.8. Calcd. for $CoPc(CONH_2)_4$: C 58.14,

N 22.61, Co 7.9; atomic ratios: C/N = 3.00, N/Co = 12.0. Characterization by IR see Fig. 1a.

Conversion into the desired tetracarboxy-compound was carried out by boiling in 50% KOH (8-10 hrs.) and subsequent precipitation with concentrated HCl according to the method given by Boston and Bailar [14]. After purification by washing twice with 0.1 N HCl and once with, successively, acetone and ether, the product was dried during 24 hrs. (100^0C, 1 mm Hg).

Anal. Found: C 52.62, H 2.67, N 13.75, Co 6.74; C/N (atomic ratio) 4.47. Calcd. for $CoPc(COOH)_4 \cdot 4H_2O$: C 52.76, H 2.95, N 13.68, Co 7.19; C/N (atomic ratio) 4.50. IR-spectrum (Fig. 1b): 3400 cm^{-1} (b, H_2O); 3000-2500 cm^{-1} (b, COOH); 1720 (sh), 1705 (s), and 1685 cm^{-1} (s) (COOH); 1330 (s), 1085 (s), 910 (w), 775 (m) and 735 cm^{-1} (s) (characteristic CoPc-peaks). UV-spectrum: 671 nm ($\log \varepsilon$ = 4.88), 620 nm (sh) and 328 nm ($\log \varepsilon = 4.77$). $CoPc(COOH)_4$ is insoluble in water, soluble in DMF and THF.

Tetrasodiumsalt of Cobalt(II) 4, 4', 4'', 4'''-tetracarboxyphthalocyanine ($CoPc(COONa)_4$)

$CoPc(COOH)_4$ was solved in 0.1 N NaOH and the resulting tetrasodiumsalt precipitated with ethanol p.a. The precipitate was collected with the aid of a centrifuge and washed with ethanol and aceton and finally dried during 24 hrs. (100^0C, 1 mm Hg).

Anal. Found: C 43.83, H 2.96, N 11.43, Co 5.74; C/N (atomic ratio) 4.47. Calcd. for $CoPc(COONa)_4 \cdot 8H_2O$: C 44.13, H 2.88, N 11.44, Co 6.02; C/N (atomic ratio: 4.50). IR-spectrum (Fig. 1c): 3400 cm^{-1} (b) (H_2O); 1610 (s), 1560 (s), and 1375 cm^{-1} (s) (COO^-); 1325 (s), 1085 (m), 785 (m) and 735 cm^{-1} (s) (characteristic CoPc-peaks).

Tetrasodiumsalt of Cobalt(II) 4, 4', 4'', 4'''-tetrasulfophthalocyanine ($CoPc(SO_3Na)_4$

The preparation of this compound was as described in a previous paper [9].

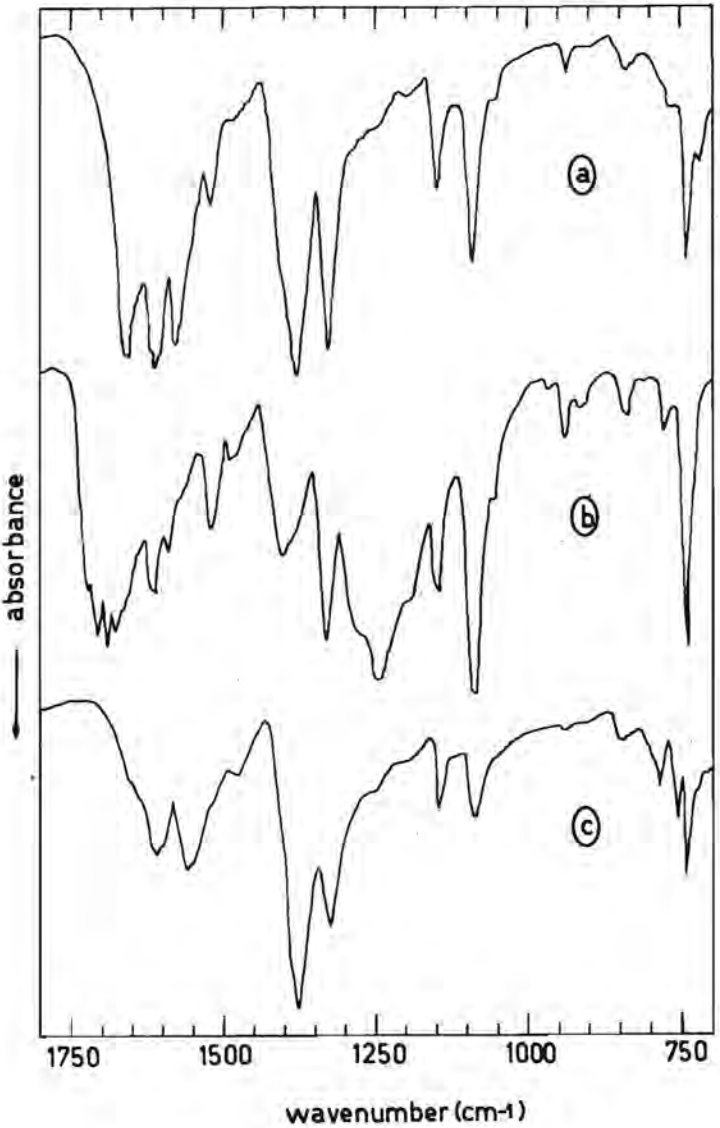


Fig. 1. IR-spectra of substituted cobalt(II)-phthalocyanines: (a) $CoPc(CONH_2)_4$, (b) $CoPc(COOH)_4$, (c) $CoPc(COONa)_4$.

Coupling of CoPc and PVAm

a. Coupling by complexation. Prior to addition of mercaptan, aqueous solutions of PVAm and CoPc were brought together in the reaction vessel in which the catalytic activity measurements were performed. Generally, a complexing time of 40 minutes was applied before the substrate 2-mercaptoethanol was added.

b. Covalent coupling. Covalent polymer attachment was achieved by a carbodiimide-promoted condensation reaction [15, 16]. A typical coupling experiment was performed in the following way: 0.9 mg (1.1 μmol) $CoPc(COOH)_4$ and 6.5 mg (32 μmol) dicyclohexyl-carbodiimide (DCCI) were, successively, added to 300 mg PVAm-HCl suspended in 15 ml THF (p.a., dried before use on CaH_2). After stirring the reaction mixture for about 48 hours at ambient temperature, the coupling product was collected by means of centrifugation. The solid product was extracted extensively with DMF until a colourless wash liquid resulted, whereupon three extractions with THF were carried out. In this way 295 mg of a blue coloured product could be obtained.

HCl was removed from the product as described before for unmodified PVAm-HCl. The amount of HCl-free coupling product so obtained was 140 mg. Cobalt-content was 0.0129%, *i.e.* 28% of the introduced CoPc has been attached to the polymer. The IR-spectrum of the coupling product is identical to that of unmodified PVAm [12]. The same experiment in THF without DCCI resulted in a colourless product (after extraction with DMF and THF); no coupling was achieved under these conditions.

Activity measurements

Activity measurements were carried out in an all-glass, thermostated ($T = 23^0C$), double-walled Warburg apparatus provided with a mechanical (glass-)stirrer. The rate of oxidation was determined by measuring the rate of consumption of the first 20 ml of oxygen at constant oxygen pressure ($P(O_2) = 1$ atm.) and a constant stirring speed ($v_s =$ 3000 r.p.m.). Because of this high stirring speed, no oxygen transport limitations were observed. Unless otherwise stated water was used as the solvent; total reaction volume 75 ml. The amount of catalyst was chosen in such a way that an appropriate rate of oxygen consumption resulted (0.5 - 10.0 ml/min.). The substrate, 2-mercapto-ethanol (Merck) was distilled before use and kept under nitrogen. Accumulated H_2O_2 was analyzed spectrophotometrically using $TiCl_3$-H_2O_2 as reagent [17].

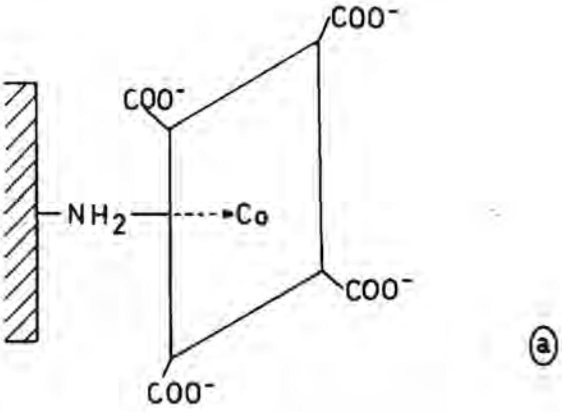
Instrumentation

IR spectra were recorded on Hitachi EPI G and Grubbs-Parson IR-spectrophotometers using KBr-pellets. Optical spectra were measured with an Unicam SP 800 spectrophotometer. ESR-spectra were recorded on a Varian E-15 ESR-spectrometer with E-101 microwave bridge (X-band) and a V-4540 variable temperature controller. A Hewlett Packard (Model 185) apparatus has been used for C, H, N analysis (*in duplo*). Co-contents were determined *in duplo* by means of neutron activation analysis using a Ge (Li)-semiconductor detector. Viscosity measurements were carried out with a Hewlett Packard automatic solution viscosimeter of the Ubbelohde type.

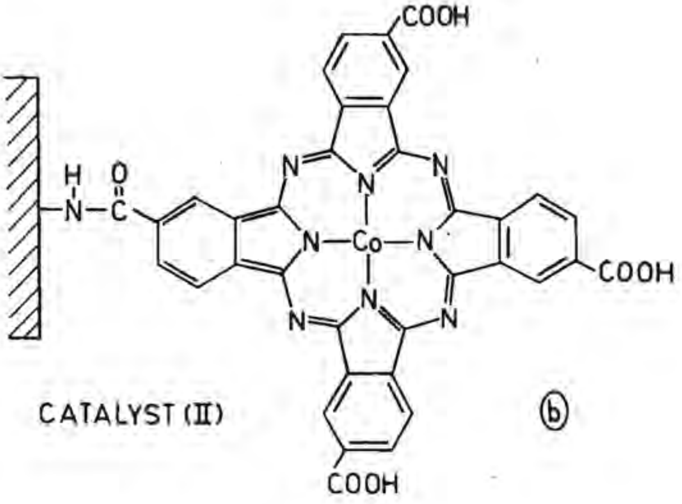
3. Results

A. *Characterization of the catalysts*

Gaspard *et al.*[18] suggest that the ammoniumsalt of the tetracarboxy-phthalocyanine can be obtained using trimellitic acid as the starting material. Our findings are at variance with this assignment, as the product composition could not be modified by treatment with strong acid. In addition the IR-spectrum of the product (*see* Fig. 1a) shows specific amide-bands (1660, 1620, and 1580 cm^{-1}) and lacks bands in the 1675-1750 cm^{-1} region characteristic of aromatic carboxy-groups [14]. These results and the elemental analysis of the product (*see* experimental) give strong indication that in fact the obtained product should be characterized as the cobalt(II) 4, 4', 4'', 4'''-tetraamide-phthalocyanine ($CoPc(CONH_2)_4$).



CATALYST (I)



CATALYST (II)

Fig. 2. Polymer attachment of tetracarboxy cobalt-phthalocyanine: (a) by complexation (catalyst I), (b) by formation of a peptide linkage (catalyst II).

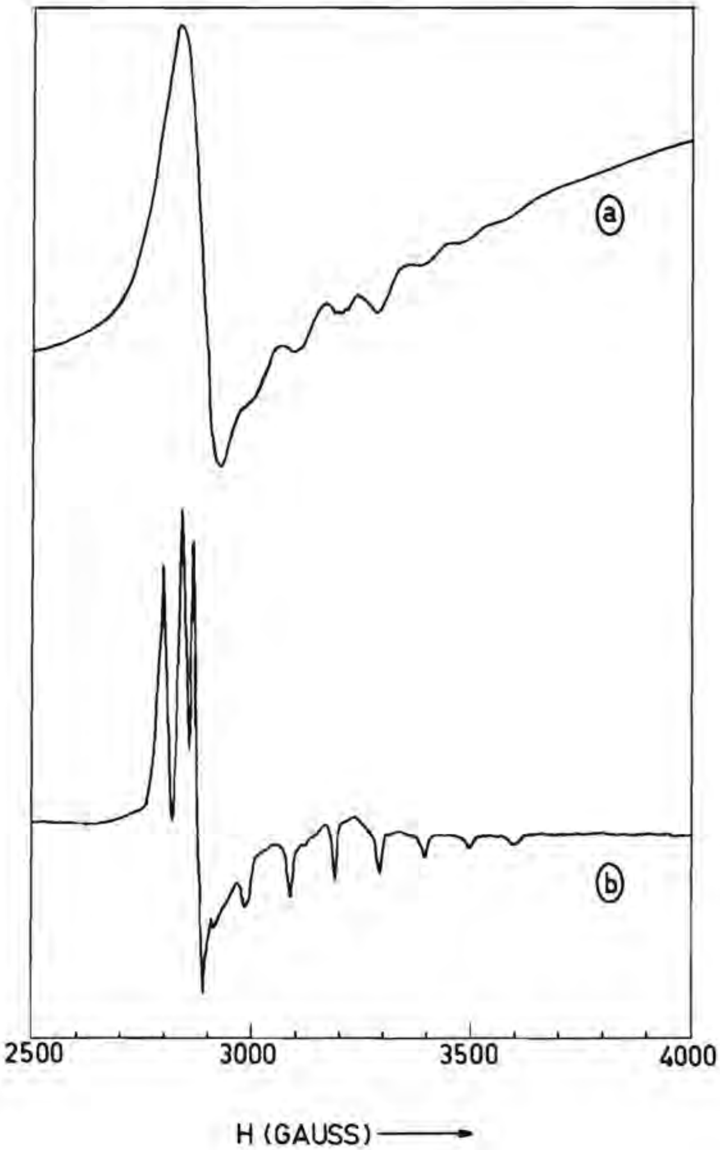


Fig. 3. ESR-spectra (recorded at -140°C) of
(a) CoPc(COOH)$_4$/PVAm comples suspended in DMF and
(b) CoPc(COONa)$_4$ dissolved in DMF.

The desired $CoPc(COOH)_4$ could be obtained by hydrolysis of $CoPc(CONH_2)_4$ in 50% KOH [14]. The IR-spectrum of $CoPc(COOH)_4$ (*see* Fig. 1b) reveals bands characteristic of aromatic carboxy-groups (1720, 1705, and 1685 cm^{-1}).
$CoPc(COONa)_4$ was prepared in a simple way by dissolving the $CoPc(COOH)_4$ in 0.1 N NaOH and subsequent precipitation in ethanol. The IR-spectrum of the tetrasodiumsalt is shown in Fig. 1c.

As reported in the experimental part two different types of catalysts were prepared. In the following it will be demonstrated that although of similar composition, these two are indeed structurally different. When a solution of $CoPc(COOH)_4$ is added to PVAm (in solution or in the solid state) complex formation is observed. Besides dipolar interactions between COOH-substituents of the phthalocyanine and polymeric amine groups, an important contribution to the binding should be ascribed to a coordinative interaction between polymeric amine groups and the central metal atom of the phthalocyanine (Fig. 2a, catalyst I). Conclusive evidence of this so-called axial coordination was obtained from ESR measurements on $CoPc(COOH)_4$/PVAm complexes suspended in DMF. After extensive evacuation to eliminate oxygen adducts, a well-resolved ESR signal could be observed exhibiting a distinct ^{14}N superhyperfine tripletsplitting on one of the central parallel Co hyperfine absorptions (Fig. 3a). In addition the overall picture of the signal is quite typical of 5-coordinate cobalt complexes [19] and differs appreciably from the signal of $CoPc(COONa)_4$ dissolved in DMF in the absence of PVAm (Fig. 3b). These results reveal the existence of a bonding interaction between one polymeric amine group and the cobalt centre of the phthalocyanine. Similar interactions between low molecular N-bases and planar Co-compounds are well known in the literature [19] and have been fairly thoroughly studied because of their biological relevance [20].

It should be stressed that complexation does not occur when the amine carrier is in the salt form, as could be shown experimentally. On the other hand the formation of a peptide linkage in the presence of dicyclohexyl-carbodiimide (DCCI)

TABLE 1 Catalytic activities of substituted cobalt-phthalocyanines in aqueous media.

NaOH (mmol)	$[RS^-]/([RSH] + [RS^-])$	spec. rate (ml min^{-1} µmol Co^{-1})	
		$CoPc(SO_3Na)_4$	$CoPc(COONa)_4$
0	0.00	4.1	3.6
1	0.07	11.3	8.8
2	0.14	15.1	15.6
6	0.42	45.4	48.8
10	0.70	60.6	58.8
15	1.00	16.1	15.2

reaction conditions: see experimental, $2 \cdot 10^{-7}$ mol CoPc, substrate: 2-mercapto-ethanol (1ml, 14.25 mmol).

will be favoured, when the hydrogen salt of PVAm (PVAm-HCl) is used [15]. Hence, in this case application of DCCI necessarily results in formation of a peptide-linkage between an amine-group of the polymer and one or more carboxy-group(s) of $CoPc(COOH)_4$ (*see* Fig. 2b, catalyst II). It should be noted, that this catalyst has to be desalted prior to its use in a catalytic experiment. It will be obvious that after this removal of bonded HCl, apart from the peptide linkage, also a coordinative cobalt-amine bond may be expected.

B. Catalytic activity measurements

Activities without polymeric base

In table 1 some results are presented which allow comparison to be made between the catalytic activities of $CoPc(SO_3Na)_4$ and $CoPc(COONa)_4$ using NaOH as the base. It appears that the activities of both catalysts are almost equal and that the actual rate is strongly dependent on the amount of base applied, completely consistent with the idea that the thiolate anion (RS^-) is the species involved in the

TABLE 2 Relative activities in successive runs of $CoPc(COONa)_4$ in aqueous media.

NaOH (mmol)	run 1	run 2*
1	1	0.78
2	1	0.56
6	1	0.40

reaction conditions: see experimental, $2 \cdot 10^{-7}$ mol CoPc, substrate: 2-mercapto-ethanol (1 ml, 14.25 mmol).

*this run carried out after completion of the previous run by adding 1 ml 2-mercapto-ethanol.

oxidation reaction. However, excess of base - e.g. 15 mmol NaOH per 14.25 mmol mercaptan - causes a loss of activity. Furthermore during any catalytic experiment such a loss of activity is observed due to a sharp rise of the pH, as soon as the amount of base exceeds the amount of unconverted thiol.

Introduction of a fresh portion of mercaptan after completion of the first run did not restore the original activity. Relative initial activities of $CoPc(COONa)_4$ in successive runs are presented in Table 2. Obviously, the reduction of reaction rate in successive runs is less pronounced as lower amounts of base are used. In contrast, for $CoPc(SO_3Na)_4$ the loss of activity in successive runs was appreciably less and did not vary with the amount of NaOH present. A combination of the results shown in Table 1 and 2 leads to the conclusion, that relatively stable $CoPc(COONa)_4$/ NaOH systems can only be obtained, when using low amounts of NaOH. However, under these conditions only low initial rates can be reached.

TABLE 3 Activities of the polymeric catalysts in aqueous media.

NaOH (mmol)*	spec. rate ($ml\ min^{-1}\ \mu mol\ Co^{-1}$)		H_2O_2 accumulation
	catalyst I**	Catalyst II***	
0.0	526	444	yes, high conc.
0.1	506	478	yes, low conc.
1.0	482	552	no
2.0	506	696	no
6.0	154	453	no
10.0	63	233	no
15.0	26	36	no

reaction conditions: see experimental,
substrate: 2-mercapto-ethanol (1 ml, 14.25 mmol).

* added 10 minutes before start of the experiment.

** $CoPc(COONa)_4$ (10^{-8} mol) coupled by complexation to PVAm (10^{-4} mol amine) with stirring; time of complexation 40 minutes.

*** $CoPc(COOH)_4$ covalently coupled to PVAm (Co-content: 0.0129%, always 5 mg was used).

Activities of bifunctional catalysts in water

The catalytic activities of catalyst I (*i.e.* $CoPc(COONa)_4$ attached by complexation to PVAm, *see* Fig. 2a) and catalyst II (*i.e.* $CoPc(COOH)_4$ covalently attached to PVAm, *see* Fig. 2b) have been investigated (*see* Table 3).
Both polymeric systems show remarkably high activities as

TABLE 4 Relative activities in successive runs of the polymeric catalysts in aqueous media.

NaOH (mmol)*	Catalyst I*		Catalyst II*		
	run 1	run 2**	run 1	run 2**	run 3**
0.0	1	0.19	1	0.39	0.09
0.1	1	0.46	1	0.51	0.25
1.0	1	0.58	1	0.65	0.48 ++
2.0	1	0.80	1	0.61	0.46
6.0	–	–+	1	0.97+++	0.66

reaction conditions: see experimental, substrate: 2-mercapto-ethanol (1 ml, 14.25 mmol).

*specifications as in table 3. **this run carried out after completion of the previous run by adding 1 ml 2-mercapto-ethanol. +not determined, see text. ++relative activities in run 4,5 and 6, respectively, are 0.42, 0.46 and 0.42. +++flattered result, see text.

compared to their polymer-free analogues. Even in the absence of alkaline base extremely high activities are attained, due to the bifunctional character of the polymeric catalysts. It appears, that the activities observed are not appreciably affected by the presence of low amounts of alkaline base, in strong contrast with polymer-free systems (*cf.* Table 1)

We could not detect a significant influence of the molecular weight of the polymer under the present conditions. The data reported in Table 3 and 4 were obtained with catalytic systems consisting of PVAm with a number average molecular weight, $\bar{M}_n$ = 21000 (determined by viscosimetry).

A disadvantage of previous polymeric systems in the absence of alkaline base was their loss of activity observed in subsequent runs [9]. The same behaviour is observed for

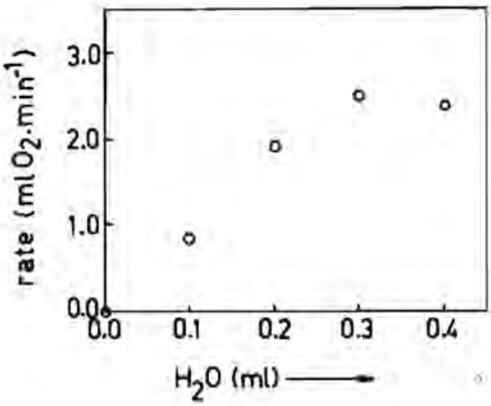


Fig. 4. Relationship between the catalytic activity of catalyst II (4.9 mg) in toluene (70 ml) and the amount of water present (substrate: 1 ml 2-mercapto-ethanol).

the bifunctional catalysts presently under investigation (*see* Table 4). This loss of activity has been ascribed to a poisoning of the basic groups of the polymer by acidic byproducts. The relative stability of the PVAm based catalysts towards alkaline base provides an opportunity for *in situ* regeneration of the polymeric base during a catalytic experiment. For both polymeric catalysts the loss of activity can be diminished by addition of NaOH. This effect is more distinct with addition of more base. Relative activities in the presence of higher amounts of NaOH were not determined as this would not be meaningful, taking into account the reduced activity values observed in the first runs (*see* Table 3, starting with 10.0 and 15.0 mmol NaOH).

Activities of bifunctional polymeric catalysts in toluene

The polymeric catalysts presented here can be applied in the sweetening-process of petroleum fractions, which involves the autoxidation of mercaptans to disulfides. These processes are usually carried out, in a two-phase system, an oil phase containing the mercaptans and an aqueous phase containing the required base [7, 8]. The polymeric catalysts do not require additional base as a promoter, so these catalysts may provide a possibility of avoiding the aqueous phase. Therefore we investigated the catalytic properties of our polymeric catalysts in an apolar medium. In addition, this gives the possibility to elucidate the role of water in the overall reaction mechanism.

Surprisingly, no activity of the bifunctional catalysts is observed in pure toluene as reaction medium. However, when a slight amount of water is added (0.1 ml) a dramatic jump in activity occurs (*see* Fig. 4). Consecutive additions of water give rise to a further increase of the catalytic activity up to a maximal value. So the presence of water appears to be essential for the catalytic activity of the bifunctional catalysts. In order to compare the activities of catalyst I and II we carried out experiments in toluene (70 ml)/H_2O (1 ml) mixtures. Observed specific rate for catalyst I (10^{-8} mol $CoPc(COONa)_4$/10^{-4} mol amine): 67 ml O_2/µmol Co. min. For catalyst II ($1.16 \cdot 10^{-8}$ mol $CoPc(COONa)_4$/$1.23 \cdot 10^{-4}$ mol amine): 442 ml O_2/µmol Co. min. The catalytic activity of catalyst II appears to be completely comparable with the activity measured in aqueous medium (*see* Table 3). The relative activities in successive runs of catalyst II in toluene (70 ml)/H_2O (1 ml) correspond with the values presented for aqueous medium (run 1:1.00, run 2: 0.47, run 3: 0.07; *cf.* Table 4).

4. Discussion

Activities of the catalysts

Whereas the promoting role of alkaline hydroxide in the systems without polymeric base is very significant, in catalytic systems with a polymeric base it is of minor importance. Only a tendency towards increased activity can be noted for the covalently bonded catalyst (II), when small amounts of NaOH are applied. This may be explained by taking into account that addition of alkaline base indeed increases the overall concentration of thiolate anions (RS^-), but it does not appreciably contribute to the relative high local RS^- concentration at the oxidation site. The non-homogeneous distribution of amine groups, inherent to the coil structure of PVAm in the dilute aqueous solution is responsible for this high local concentration of RS^- [9].

It is remarkable, that catalyst I ($CoPc(COONa)_4$) attached by complexation to PVAm) retains its activity level in the presence of low amounts of NaOH. This is in strong contrast with the behaviour reported earlier for the systems in which poly(acrylamide) modified with amine groups was used as the polymeric base [9]. In that particular case, a substantial loss of activity was observed on addition of 6 mmol NaOH due to decomposition of the polymer/CoPc complex. These phenomena are ascribed to the better complexing properties of PVAm towards CoPc resulting from the much higher density of amine groups in PVAm. Nevertheless, there are indications that also for catalyst I decomposition by NaOH is not completely avoided. Firstly, the promoting effect of low amounts of NaOH as observed for catalyst II, is not detected here. Secondly, while the use of 6 mmol NaOH gives no significant deactivation of the covalently attached catalyst (II), in the case of catalyst I a distinct fall in activity occurs. Both phenomena are explained by a partial rupture of the polymer/CoPc interaction.

The activity loss observed for both catalysts with use of more than 6 mmol NaOH (*see* Table 3) requires a further explanation. In the case of catalyst II (covalently bonded) a rupture of the CoPc/PVAm linkage by alkaline base seems not probable, as excessively high pH values cannot occur due to the buffering action of the weak acid (RSH) present. A more probable explanation can be found considering equation 3:

$$\text{Pol-}\ NH_2 + RSH \rightleftarrows \text{Pol-}\ NH_3^{+-}SR \qquad (3)$$

Pol- NH_2 represents the PVAm base. One can calculate (taking for PVAm $pK_a = 10$) with RSH representing 2-mercapto-ethanol:

$$\log \frac{[\text{Pol- NH}_3{}^{+-}\text{SR}]}{[\text{Pol- NH}_2]} = 10 - \text{pH}$$

Hence, under reaction conditions (1 ml RSH) using 10 mmol NaOH (initial pH ~ 10) the ratio $[\text{Pol- NH}_3{}^{+-}\text{SR}]/[\text{Pol- NH}_2]$ will be 1.0 and using 15 mmol NaOH (initial pH ~ 12) this ratio will be only 0.01. From this calculation we can learn that when using higher amounts of base, the thiolate anions (RS^-) will be expelled from the polymeric base. Consequently, the oxidation rate will decline because of the reduced local RS^- concentrations. Other possible effects, as for instance inhibition of the catalyst by the action of OH^- cannot be excluded at this moment. In the case of catalyst I, a rupture of the polymer/CoPc complex will certainly contribute to the sharp fall of the activity observed for higher amounts of NaOH.

Stability of catalysts

The deactivation of the $CoPc(COONa)_4$/NaOH systems and of the $CoPc(COONa)_4$/PVAm systems as observed in successive runs is affected by NaOH (*see* Table 2 and 4). However, the effect of added alkaline base on the deactivation is quite different in the two cases. In the conventional polymer-free system the deactivation is more pronounced with increasing amounts of alkaline base. On the other hand, for the polymeric systems increasing amounts of alkaline base cause improvement of the stability of the catalysts. Such an improvement could be expected assuming that the loss of activity is caused by strong sulfur containing acids poisoning the basic groups of the polymer. In the presence of NaOH an *in situ* neutralization of these acids can be obtained, so the basic groups of the polymer remain available for RS^- generation.

The results presented in Table 4 indicate that the use of NaOH cannot afford a complete protection against the deactivation of the bifunctional catalysts. This remaining loss of activity is not entirely understood, but presumably product-inhibition (by RSSR) may play a role here. The maintenance of activity observed for catalyst II, when using 6 mmol NaOH, seems remarkable. However in this case no complete conversion was attained during the first run. Consequently, the amount of mercaptan present in the initial stage of the second run was higher than usual, resulting in more favourable starting-conditions for this particular run.

The relative activities in successive runs (stabilities) of the CoPc/NaOH system and of the CoPc/PVAm systems seem to be comparable (*see* Table 2 and 4). However, a better understanding of the stability of the catalytic system is provided by considering at the same time the number of turnovers (average total number of RSH molecules converted per cobalt site) involved per run. For a typical experiment with the polymeric catalysts (10^{-8} mol CoPc and $14.25 \cdot 10^{-3}$ mol RSH) this number amounts to $1.4 \cdot 10^{6}$, while for the polymer-free catalyst ($2 \cdot 10^{-7}$ mol CoPc and $14.25 \cdot 10^{-3}$ mol RSH) this amounts to $7 \cdot 10^{4}$. Observing for both catalytic systems a similar activity loss per run, these conversion values implicate that the polymeric catalyst has a much higher total conversion capacity per cobalt site. Hence, the polymeric catalysts allow a more profitable use during their lifetime than their conventional counterpart.

As stated before alkaline base can reduce the loss of activity of the polymeric catalysts because of the *in situ* neutralization of produced sulfur containing oxo-acids. Another possibility is that the added base prevents the formation of these acids. Presumably, these acids are formed in traces by the reaction of H_2O_2 with RSH, while disulfide (RSSR) is the main product of this particular reaction. It is interesting to know, that the disulfide formation is accellerated at higher pH [21]. As a consequence at higher pH-values H_2O_2 accumulation was not detectable during the reaction (*see* Table 3). On the other hand at low pH-values (*i.e.* in the absence of NaOH or in the presence of very low amounts of NaOH) H_2O_2 accumulation was observable. It seems probable that only in the latter case sulfur containing acids are formed [21].

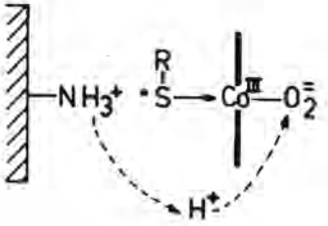


Fig. 5. An intermediate situation at the PVAm/CoPc catalyst during the autoxidation of mercaptan.

Activities of the polymeric catalysts in toluene

The results presented clearly indicate, that small amounts of water are required to obtain an active catalytic system. This phenomenon may be explained from a consideration of an intermediate situation during the catalytic autoxidation of mercaptan (*see* [9]).

At the stage depicted (Fig. 5) protonation of the coordinated oxygen has to take place for the reaction to proceed. Protonation requires an effective proton transport medium. Because of the hydrophylicity of the polymer used, added water will preferentially be in the environment of the polymer, therefore even small amounts of water are sufficient to provide the required proton transfer.

The non-ionic nature of the bonding of mercaptan to the amine carrier in an apolar medium may be another reason for the requirement of water. Such an non-ionic bonding would inhibit the formation of a sufficiently reactive thiolate anion. Such an inhibition could be avoided by using a polar organic liquid as a reaction medium. However, employment of DMF instead of toluene did not give rise to catalytic activity. This result is consistent with the idea that a suitable proton transfer medium is essential for the catalytic induced reaction.

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CHAPTER 6

MECHANISM OF THE AUTOXIDATION OF 2-MERCAPTO-ETHANOL AND CYSTEINE CATALYZED BY COBALT (II) 4, 4', 4'', 4'''-TETRASULFO-PHTHALOCYANINE IN AQUEOUS SOLUTIONS

Summary

The title complex (CoTSPc) has been used as a catalyst for the autoxidation of mercapto-ethanol and cysteine in aqueous solutions. Characterization of the cobalt complex present during the steady-state of the reaction was attempted by carrying out optical measurements during the oxidation, while additional information was obtained from ESR measurements on frozen solutions. Elucidation of the nature of the steady-state (ss) intermediate was achieved by comparing its optical spectrum with that of a variety of complexes obtained by oxidation, reduction or oxygenation of CoTSPc. It was found that independent of the exact reaction conditions, the ss-intermediate mainly observed is a binuclear peroxo adduct coordinated by thiolate anions, *viz.*

$RS^- - Co^{III}TSPc - O_2^= - Co^{III}TSPc - {}^-SR$.

Kinetic measurements, surprisingly, gave a negative order with respect to oxygen and evidence was found of a high catalytic activity of the reduced form of the catalyst ($Co^{I}TSPc$).

The optical measurements together with kinetic data point to a reaction model consisting of two parallel reaction paths for the catalyst. Oxygenation of the catalyst plays an important role in both reaction paths, but an extremely active catalyst is only obtained from oxygenation of the reduced catalyst resulting in

a mononuclear Co^{III} peroxo complex. On the other hand, oxygenation of Co^{II}TSPc gives rise to the formation of a relatively inert dimeric peroxo adduct, *i.e.* the ss-intermediate.

1. Introduction

The excellent catalytic activity of transition metal phthalocyanines in a number of redox processes is well known [1, p. 92]. These catalysts can be applied advantageously in aqueous media by introduction of dipolar substituents in the phthalocyanine ring to make them water soluble. Thus, an extremely active catalyst soluble in water is represented by Cobalt(II)-tetrasulfo-phthalocyanine (CoTSPc). Because of the excellent catalytic properties of this complex [2], the mechanism of catalytic operation in reactions as autoxidation of cysteine [3, 4], hydrazine and hydroxylamine [5] has drawn much attention.

Kundo and Keier [3] postulate a Co^{II}/Co^{I} redox mechanism for the catalytic process involving autoxidation of cysteine to the disulfide cystine. Their reaction model is based largely on optical measurements of the reduction of the catalyst by cysteine in an oxygen-free alkaline medium. The superior catalytic activity of CoTSPc is explained from the ability of the cobalt complex to undergo reduction more easily than any other metal phthalocyanine. The important role of reducibility is supported by the positive relation found between the catalytic activity of a variety of substituted cobalt phthalocyanines and their ease of reduction by the substrate [6]. Moreover, stabilization of the Co^{III} oxidation state by addition of cyanide ions leads to a significant increase of reduction time and connected herewith a substantially lower catalytic activity in the autoxidation reaction.

Later on, Wagnerová *et al.* [7] and Gruen and

Blagrove [8] demonstrated by means of optical spectra the ability of CoTSPc to form a stable adduct with oxygen under alkaline conditions. Manometric measurements carried out by Wagnerová *et al.* [9] showed a stoichiometry of $Co/O_2 = 2/1$ for the resulting product of oxygenation, indicating the formation of a binuclear dioxygen adduct ($L.Co.O_2.Co.L$). Wagnerová *et al.* [5a] come to the conclusion that catalytic activity in oxidation reactions is only exhibited by those metal complexes able to form oxygen adducts. The reactive intermediate was suggested by them to be a ternary cobalt complex with coordinated O_2 and substrate S (*viz.* $S.CoTSPc.O_2$), a conclusion largely based on kinetic experiments. The electron transfer leading to oxidation of the substrate is assumed to take place within the complex without alteration of the valence state of the mediating cobalt centre (Co^{II}).

It should be noted that formation of the *binuclear* oxygen adduct was not taken into consideration by Wagnerová *et al.* largely because of its slow rate of formation under the pH condition applied. However, as stated by the authors [5b], the rate of oxygenation is evidently dependent on the nature of the ligand occupying the 5th (axial) position of CoTSPc. Therefore, formation of the binuclear oxygen adduct under catalytic conditions should not be ruled out *a priori*. In fact, it was pointed out by Wagnerová *et al.* [9] that the rate determining step in the production of the binuclear oxygen adduct is reaction (i) (L being an axial ligand):

$$L.CoTSPc + O_2 \xrightarrow{OH^-} L.CoTSPc.O_2 \qquad (i)$$

$$L.CoTSPc.O_2 + L.CoTSPc \rightarrow L.CoTSPc.O_2.CoTSPc.L \qquad (ii)$$

Hence, the formation of a ternary complex during the catalytic reaction (i) renders the formation of the binuclear oxygen adduct (ii) even more probable.

Optical measurements during the steady-state of the autoxidation reaction might enable the identification of intermediate complexes present in the solution. This would be helpfull in solving the question on the presence of a binuclear oxygen adduct under reaction conditions. Unfortunately, Kundo and Keier [3] and also Wagnerová [5a] only recorded spectra of the reduction product (*viz.* Co^ITSPc) and of the product after oxygenation. No optical spectra during the catalytic reaction, *i.e.* in the presence of both thiol and oxygen, were presented.

An attempt to elucidate the valence state of the cobalt complex during the reaction was made by Smith *et al.* [10] using ESR spectroscopy. Frozen solutions of oxygenated CoTSPc showed the characteristic 1:1 O_2 adduct signal and in the absence of oxygen using hydrazine or hydroxylamine as the substrate clear evidence of cobalt-substrate interaction was found from the ^{14}N triplet splitting observed.
However, those ESR measurements as carried out under catalytic conditions are of limited value because of the extremely high CoTSPc concentration applied. The latter will cause an excessive high rate of oxidation, without doubt leading to severe oxygen depletion and probably resulting in almost anaerobic conditions. It may be expected that under such conditions reduction of Co^{II} to Co^I takes place, as was in fact observed by these authors. Thus it is doubtful whether the observations made by Smith *et al.* [10] do answer the question on the identity of the intermediate present under realistic conditions of the autoxidation reaction.

In view of the discrepancy between the reaction models as suggested by Kundo and Keier [3] and by Wagnerová *et al.* [4], we have undertaken a study to distinguish among these mechanistic possibilities. Our first object was to elucidate the identity of the intermediate present during the steady-state (ss) of the autoxidation reaction. Therefore, we carried out optical measurements during the catalytic process under conditions that no oxygen depletion occurred. For identification purposes ss-spectra were compared with a variety of spectra obtained using electrochemical and chemical techniques. Knowledge of the nature of the ss-intermediate may provide a valuable tool in the elucidation of the reaction mechanism, but it should be stressed that it does not necessarily answer the question as to the identity of the *reactive* catalytic species. In this connection we should recognize that the very reason of the accumulation of the ss-intermediate is its relative stability. As a consequence, kinetic measurements are essential to evaluate the role of the ss-intermediate in the overall mechanism. Our second object, therefore, was to examine the kinetics of the oxidation reaction. The results found point to a mechanism in which the ss-intermediate - being a binuclear peroxo adduct - in fact functions as a sink for the catalytic active species. The proposed scheme predicts that an extremely active catalyst can be obtained if dimerization into the binuclear peroxo adduct is avoided for instance by polymer attachment of the catalyst.

2. Experimental

Activity measurements

The preparation of cobalt(II) 4, 4', 4'', 4'''-tetrasulfo-phthalocyanine (CoTSPc) and the equipment used for the oxidation experiments performed at 1 atm oxygen pressure have been described before, respectively, in [11] and [12].

Experiments at elevated pressure, *viz.* 1.2, 3, 5 atm were carried out in a double-walled glas reactor equipped with a sample valve for addition of mercaptoethanol (ME). A Hastings mass-flow meter was applied to determine the rate of oxygen addition to keep pressure constant in the reactor. The maximum flow measured was taken as the rate of oxygen consumption after correction for the rate measured in the absence of CoTSPc.

Activity measurements were performed under vigorous stirring; the total volume of the reaction solution was 150 ml, containing 2 ml ME (distilled before use), 12 ml 1.0 N NaOH and a variable amount of CoTSPc; $T = 21.5^0C$.

IR analysis of the reaction product and the stoichiometry of the reaction shows that exclusively the disulfide (RSSR) is formed. Complete conversion is achieved at an oxygen pressure of 1.0 and 1.2 atm but at higher pressures decay of the catalyst occurs and complete conversion is no longer achieved. No evidence was found for accumulation of H_2O_2.

Optical measurements

A Unicam *UV* spectrophotometer (SP-800 D) was used. If necessary, solutions were kept under nitrogen during the measurements. Steady-state spectra were obtained utilizing a circulation system involving the optical flow-cell. In these experiments, the total volume of the reaction solution amounted to 300 ml, there being about 50 ml in the circulation system and the remainder in the reaction vessel. Circulation of the solution was effected by means of a teflon coated Saturn pump type SPM-100 (flow ranging from 200 to 750 ml/min). Maximal flow rates were usually applied in order to avoid oxygen depletion of the solution in the optical cell.

ESR measurements

A varian E-15 X-band ESR spectrometer equipped with a V-4540 variable temp. controller served for the low temperature ESR measurements.

Electrochemical oxidation/reduction

A H-shaped electrolysis cell provided with a glass-fritt separating the two compartments was used. A Wenking potentiostat served to control the potential difference between the platinum electrodes and a saturated calomel electrode.

Electrochemical oxidation (or reduction) experiments were carried out on 2×10^{-5} M CoTSPc solutions in DMF using 0.1 M tetraethyl-ammoniumperchlorate (TEAP) as supporting electrolyte (total volume ~ 100 ml). Solutions were purged of oxygen by passing through purified nitrogen for 10 min. Also during the redox reaction nitrogen was bubbled through and a N_2 blanket was kept over the solution. A check on the completion of the redox reactions (*viz.* $Co^{II} \longrightarrow Co^{I}$ and $Co^{II} \longrightarrow Co^{III}$) was obtained from ESR recordings on the frozen solutions.

3. Results

Kinetic measurements

It is well-known that the oxidation of mercaptans by oxygen is facilitated by the presence of base [13]. We have determined the influence of NaOH addition on the rate of autoxidation of mercapto-ethanol (ME) catalyzed by cobalt-tetrasulfo-phthalocyanine (CoTSPc). As shown in Fig. 1, the rate of oxidation of ME, as measured by the O_2 uptake at constant pressure $P(O_2) = 1$ atm), indeed strongly depends on the amount of base used and increases up to a ratio of NaOH/ME ~ 0.8. The decline of activity observed at higher pH values is noteworthy being quite similar to that reported for the oxidation of cysteine using the same catalyst [4]. The

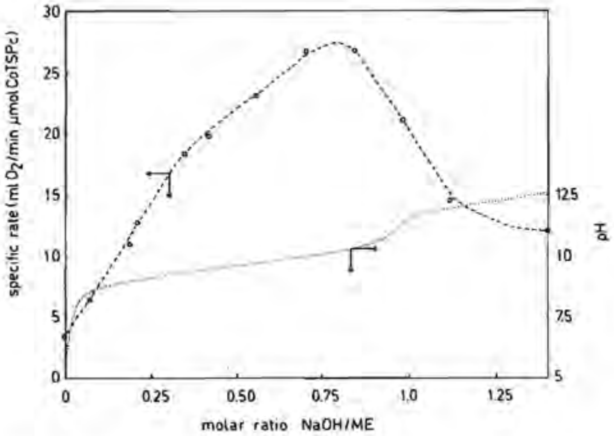


Fig. 1. Specific rate of oxidation of mercaptoethanol (ME) as a function of the amount of base in aqueous solutions (V = 150 ml, 1.5×10^{-7} mol CoTSPc, 1 ml ME (= 14.25 mmol); $P(O_2)$ = 740 mmHg, T = 24°C).

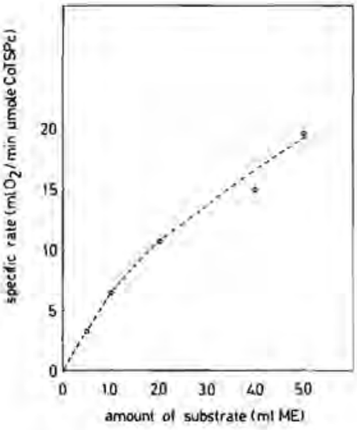


Fig. 2. Rate dependence on the amount of substrate (molar ratio NaOH/ME = 0.035; other conditions as given in Fig. 1).

TABLE 1
Specific Rate as a function of amount of catalyst and oxygen pressure

CoTSPc	Specific Rate* (mmoles O_2)/min.μmole Co			
(μmoles)	PO_2 = 1.0 atm	1.2 atm	3.0 atm	5.0 atm
0.05	.94	.88	.48	.40
0.10	.95	.84	.54	.42
0.15	1.03	.80	.59	.53
0.20	1.12	.99	.64	.52
0.25	-	1.06	.73	.54
0.35	-	1.35	-	.61
0.50	1.78	1.59	.77	.73
0.75	-	-	.87	.71

*Exp. conditions: reaction carried out in aqueous
solution, total volume 150 ml,
$T = 21.5^{\circ}C$
Substrate: 2 ml ME (28.5 mmoles),
12 mmoles of NaOH.

dependence of the rate on the amount of substrate as shown in Fig. 2 is not linear.

The order with respect to CoTSPc appears to be close to 1 in the lower concentration range as seen from the values of the specific rate (= rate per μmole of catalyst) (Table 1). At higher concentrations the values become less reliable due to the high rates of oxygen consumption. For instance, the value of 1.78 found while using 0.50 μmoles of catalyst at $P(O_2)$ = 1 atm corresponds with an actual O_2 consumption of 22.2 $ml.min^{-1}$. Under such extreme conditions and despite vigorous stirring, problems concerning gas to liquid transport of oxygen can be expected. The resulting partial oxygen depletion will give rise to an enhancement of the specific rate in agreement with the reported data. This is the consequence of the remarkable rate dependency on the oxygen pressure. As shown in Table 1, the rate of oxydation *diminishes* with *increasing* oxygen pressure. A phenomenon closely related to the observed negative order in oxygen will be discussed now; it will afford a better understanding of this peculiar behaviour.

As stated in the experimental, liquid circulation experiments were carried out during the oxidation reaction in order to find evidence on the nature of the steady-state (ss) intermediate. In that case, high flow rates were applied to avoid oxygen depletion in the circulation system containing the optical cell and to ascertain that the recorded optical spectra reflect the actual state of the catalyst under reaction conditions. Apart from these experiments - discussed later - it will be obvious that, alternatively, liquid circulation experiments provide the opportunity to let reduce the catalyst present in the circulation loop during the reaction and to examine the kinetic effect of a partial reduction of the catalyst. For instance, stopping the flow during the oxidation of ME (NaOH/Me = 0.70) gives rise to oxygen depletion in the circulation system resulting in reduction of the catalyst, which becomes manifest from the yellow colour of the solution. If subsequently the circulation is started again, but with a moderate flow rate (~ 200 ml/min), we observe a maintenance of the yellow colour of the liquid in the circulation system. So, it may be concluded that the reduction process continues to occur under flow conditions. At the same time, the flow of the yellow liquid into the stirred reactor did not alter the blue/green colour of the solution present in the reactor, indicating that only a small fraction of the catalyst in the stirred solution remained in the reduced state.

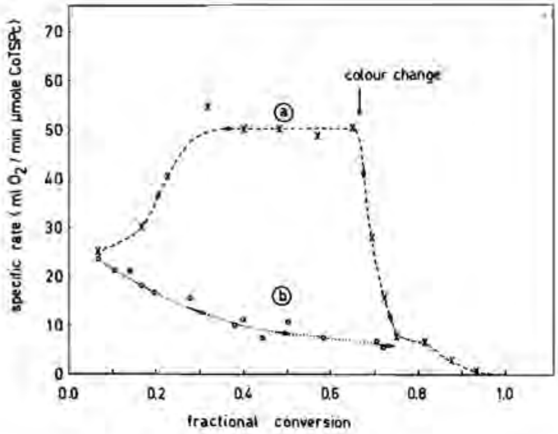


Fig. 3. The effect of partial reduction of the catalyst on its activity. Depicted are the rates of oxidation measured in the course of a run for, respectively, recirculation exp. (a) and (b) (V = 300 ml, 3 × 10^{-7} mol CoTSPc, 28.5 mmol ME, 20 mmol NaOH; P(O_2) = 740 mmHg, T = 24°C).

(a) Reduction of the catalyst in the circulation loop, initiated at the start of the reaction, is retained during the autoxidation reaction (flow rate 200 ml/min). The arrow is indicating the termination of this reduction process.

(b) Rates measured under conditions that reduction of the catalyst does not take place (flow rate 600 ml/min).

Very important now is the observation that the steady supply of reduced catalyst to the reacting solution had a dramatic effect on the rate of oxygen absorption as shown in Fig. 3. In run (a), reduction of the catalyst in the circulation loop initiated at the start of the reaction gives rise to a remarkable enhancement of the rate of oxidation. The high rate is maintained as long as reduction continues to take place

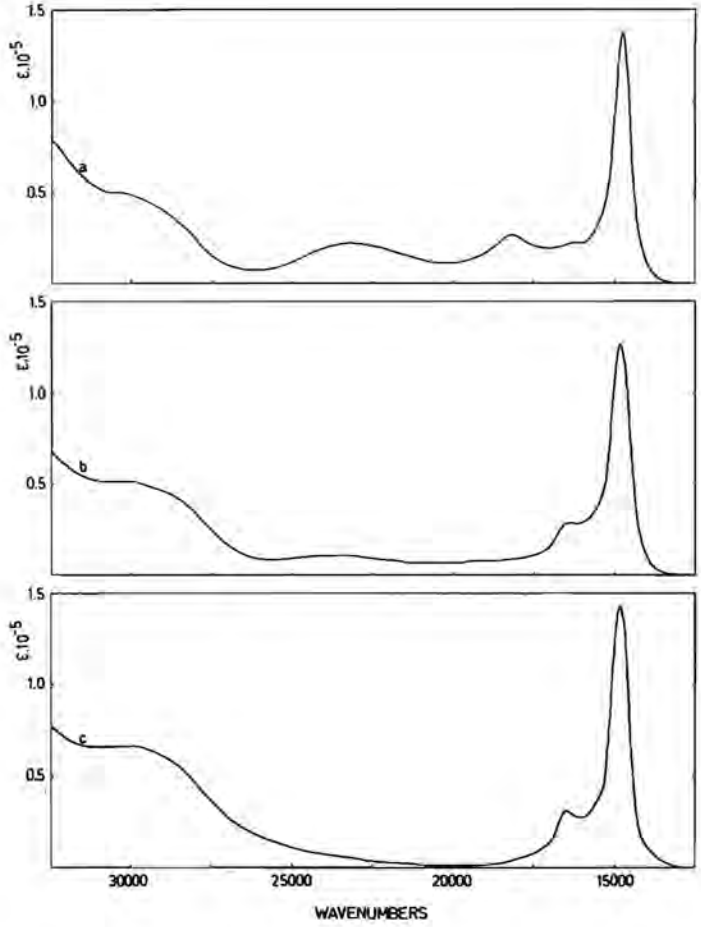


Fig. 4. Steady-state spectra in dimethylformamide and in water ($P(O_2)$ = 740 mmHg, T = 24°C).

(a) Oxidation of ME in DMF (V = 20 ml, 2 × 10^{-6} mol CoTSPc, 1 ml ME; opt. cell: d = 1 mm).

(b) Oxidation of ME in water (V = 300 ml, 6 × 10^{-7} mol CoTSPc, 28.5 mmol ME, 1 mmol NaOH; d = 50 mm).

(c) Oxidation of cysteine in water (V ; 300 ml, 6 × 10^{-7} mol CoTSPc, 1.0 g cysteine + 0.33 g NaOH (pH ~ 10); d = 50 mm).

in the circulation system. Termination of the reduction process (*see* arrow) is accompanied by a serious decline of catalytic activity. The tremendous effect of partial reduction of the catalyst is shown by comparison with the rate observed during an experiment in which no reduction takes place (b).

It should be noted that no influence of oxygen pressure on the rate of oxidation was detected when using very low amounts of base (*i.e.* NaOH/ME = 0.035). Hence, in this case the order with respect to O_2 is 0. On the other hand, the order in CoTSPc was the same (*i.e.* 1) as observed when using higher amounts of base.

Spectroscopic measurements

Steady-state (ss) spectra were recorded using a liquid circulation technique as described in the experimental section. The optical spectrum observed during the autoxidation of ME (mercapto-ethanol) in aqueous alkaline media is shown in Fig. 4b. The spectrum is characteristic for metal phthalocyanines, *viz.* a very intensive peak in the visible region with a shoulder on the high-energy side ($\nu = 14.85$ kK, $\varepsilon = 1.28 \times 10^5$ and $\nu = 16.5$, $\varepsilon = 0.30 \times 10^5$), and a broad absorption band in the *Near UV* region. The ss-spectrum shows additional bands of lower intensity at ~ 19 and ~ 23.5 kK, usually absent in spectra of $Co^{II}Pc$. A similar spectrum is observed during the autoxidation of cysteine (Fig. 4c) but in that case no band in the 19 kK region is seen.

Spectral features of the ss-spectra recorded during the oxidation of ME are practically independent of the amount of alkali added. However, in the absence of base, bands at 19 and 23.5 kK are lacking. Usually, ss-spectra appeared immediately after start of the reaction. But in case that no base was added, only a slow transformation of the originally predominant dimer spectrum (Fig. 6b) into the final ss-spectrum occurred, a process requiring about half an hour.

Because of the extremely high activity of the catalyst, only low concentrations were applied to avoid diffusional limitations of oxygen transfer into the liquid. Nevertheless, a distinct optical spectrum could be detected due to the extremely high extinction coefficients of the optical bands of metal phthalocyanines [ref. 1, p. 67]. The low concentration of catalyst does seriously restrict the possibility of an alternative way of identification, *i.e.* by ESR spectroscopy. Moreover, the formation of dimers usually occurring in aqueous media [8, 14, 15] imposes further restrictions on the utility of ESR spectroscopy. These restrictions could, however, be avoided by operation in pure DMF (without base). The reaction rate per cobalt atom proved to be much lower in this solvent, thus enabling the application of a higher catalyst concentration. Moreover, the ss-spectrum in DMF is similar to that in water (Fig. 4a, b). Furthermore, dimer formation of CoTSPc does not occur in DMF [16]. Hence, use of DMF as the solvent provides the opportunity to study the ss-intermediate also by ESR spectroscopy and to compare data with earlier ESR experiments on CoTSPc [16, 17].

Surprisingly, after rapid-freezing of a sample during the autoxidation of ME in DMF, no ESR signal was observed. After standing at room temperature *without shaking* during about half an hour and then refreezing the sample, the typical ESR signal [16] of Co^{II}TSPc with hyperfine splitting due to ^{59}Co $(I = 7/2)$ was detected. No evidence of any formation of the 1:1 O_2 adduct was found indicating that the observed transformation into the Co^{II} complex occurred after complete depletion of the oxygen solved.

Assignment of the optical ss-spectra observed in DMF and water is certainly not possible without the use of reference spectra for comparison. In view of this, oxidation and reduction products of CoTSPc were prepared and characterized by their optical spectra and in some cases by their ESR signals.

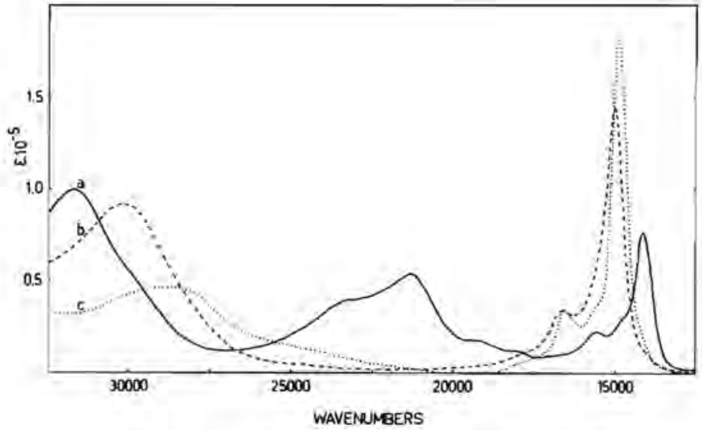


Fig. 5. Optical spectra as a function of the oxidation state of cobalt, recorded in DMF (2 × 10^{-5} M, d = 5 mm).
(a) Co^{I}TSPc, (b) Co^{II}TSPc, (c) Co^{III}TSPc.

Solutions of Co^{I}TSPc and Co^{III}TSPc in DMF could be prepared electrochemically from the parent compound Co^{II}TSPc under anaerobic conditions. As is shown in Fig. 5, marked alterations in the optical spectra are associated with a change of valence state of the cobalt centre. In particular, the optical spectrum exhibited by Co^{I}TSPc (Fig. 5a) is quite distinct from those of Co^{II} and Co^{III}TSPc. Its signal is characterized by a relatively weak low-energy band ($\nu = 14.15$ kK, $\varepsilon = 0.75 \times 10^5$) and two bands in 20-25 region (21.2 kK, $\varepsilon = 0.51 \times 10^5$ and 23.2 kK, $\varepsilon = 0.37 \times 10^5$), completely consistent with data given in the literature [18, 19]. A chemical reduction of Co^{II}TSPc in DMF by the action of ME in the presence of some alkaline base (NaOH) led to the same optical signal.

As already reported by Gruen *et al.* [8], an aqueous solution of Co^{II}TSPc manifests itself as a monomer/dimer mixture, the ratio depending on its concentration, the temperature and electrolyte concentration. Catalyst concentrations applied for the autoxidation experiments

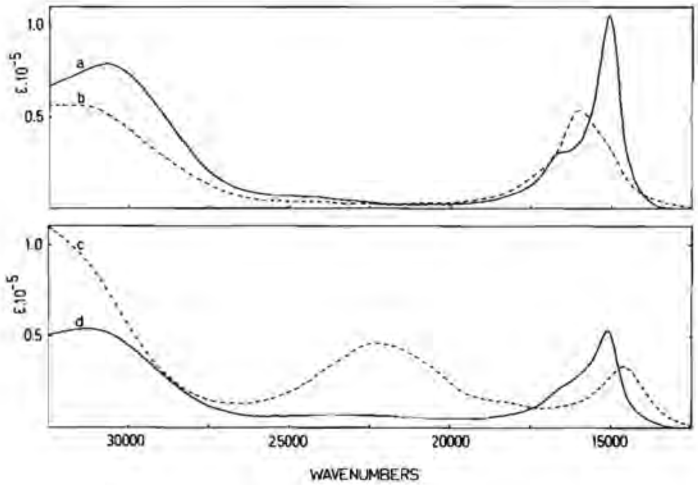


Fig. 6. Optical spectra of CoTSPc in aqueous solutions.
(a) Monomer spectrum recorded in $H_2O/DMF = 90/10$ $(2 \times 10^{-6}$ *M CoTSPc; d = 50 mm).*
(b) Dimer spectrum recorded in 0.1 M KCl solution $(10^{-4}$ *M CoTSPc; d = 1 mm).*
(c) Product from the interaction of ME with CoTSPc in the presence of NaOH obtained under anaerobic conditions (NaOH/Me ratio ~ 0.7, 2×10^{-6} *M CoTSPc; d = 50 mm).*
(d) CoTSPc/ME interaction product in the absence of base and O_2*.*

(*i.e.* 2×10^{-6}M) gave rise to the appearance of predominantly the dimer signal. In Fig. 6a and b the spectra are shown of the monomer (a) obtained in an aqueous DMF solution ($DMF/H_2O = 10/90$) and that of the dimer as observed in a 0.1 M KCl solution. In aqueous solutions no electrochemically induced reduction of Co^{II}TSPc was achieved, presumably due to the more facile electrolysis of water. But chemical reduction of Co^{II}TSPc generating Co^{I}TSPc appeared to be possible using reducing agents as cysteine, mercaptoethanol, or hydrazine, in the presence of alkaline

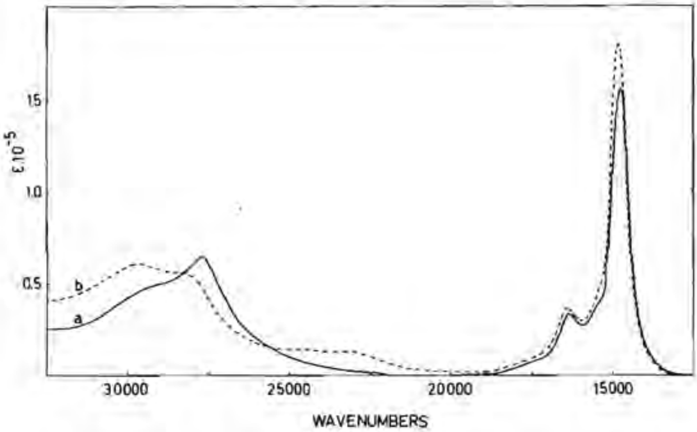


Fig. 7. Products obtained from the interaction of CoTSPc (2×10^{-5} M) with oxygen in DMF (d = 5 mm).
(a) Spectrum of the binuclear peroxo adduct ($NH_3.Co^{III}.O_2^{=}.Co^{III}.NH_3$) obtained from oxygenation of Co^{II}TSPc in the presence of NH_3.
(b) Spectrum recorded after reoxidation of electrochemically prepared Co^{I}TSPc.

base (Fig. 6c). Without base, apparently no reduction takes place as deduced from the absence of the characteristic absorption in the 20-25 region (Fig. 6d).

We have reported previously [17] that oxygenation of a Co^{II}TSPc solution in DMF in the presence of NH_3 gives rise to formation of the diamagnetic binuclear peroxo adduct ($NH_3.Co^{III}.O_2^{=}.Co^{III}.NH_3$) exhibiting a characteristic band at 27.9 kK. Oxygenation of electrochemically generated Co^{I}TSPc in DMF gives rise to the optical signal as shown in Fig. 7b. Evidently no reoxidation to Co^{II}TSPc has taken place but the identity of the oxygenated product formed is not clear. Examination of the solution by ESR spectroscopy reveals a signal with the characteristic envelope of the $Co^{III}O_2^{-}$ 1:1 O_2 adduct. No hyperfine splitting could be observed due to poor resolution. A similar

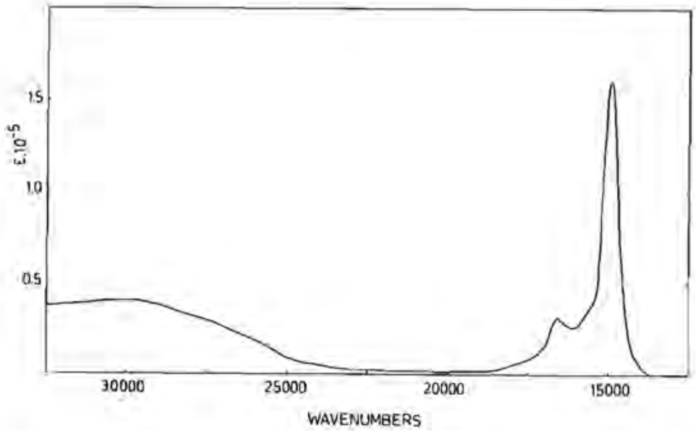


Fig. 8. Product from Co^{II}*TSPc and* H_2O_2 *in the presence of NaOH. Spectrum recorded in aqueous solution (2 ×* 10^{-6} *M CoTSPc, 2 ×* 10^{-2} *M NaOH, 0.35 M* H_2O_2*; d = 50 mm).*

reaction was recently reported for other Co^{I}-macrocyclic complexes [20] but also in that case the identity of the product formed remained obscure.

In addition to the oxygenation experiments, use of H_2O_2 as oxidizing agent might provide an alternative way to produce peroxo-adducts of CoTSPc. By carrying out such experiments, it appeared that the reaction of CoTSPc with H_2O_2 under alkaline conditions resulted in a rather stable product exhibiting the spectrum shown in Fig. 8. Apart from the intensive peak in the 15 kK region, it is characterized by a relatively low intensity of the *N.UV* band. The spectrum proves to be practically the same as that observed for Co^{III}TSPc in DMF (Fig. 5). We therefore assume that the spectrum shown in Fig. 8 represents Co^{III}TSPc in aqueous solution. This assumption is supported by findings reported by Fleischer and Cheung on cobalt porphyrins [21] who were able to oxidize Co^{II} porphyrin into the Co^{III} complex by means of H_2O_2.

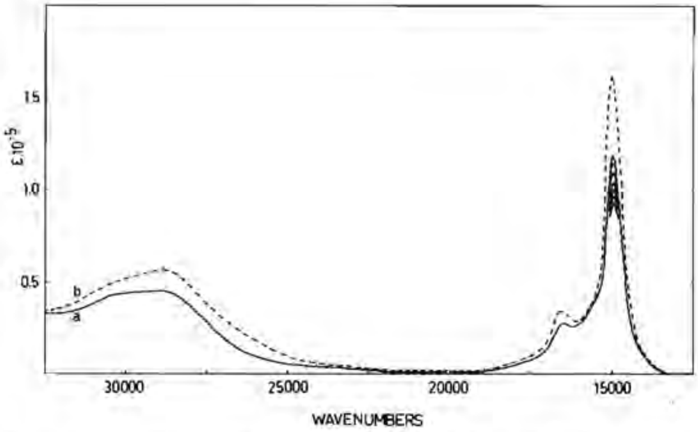


Fig. 9. Product from CoTSPc and H_2O_2 *under neutral conditions compared with a binuclear peroxo adduct in aqueous solution.*

(a) Spectrum obtained after neutralization (via H_2SO_4*) of the solution described in Fig. 8. The top of the main peak was recorded with intervals of 2 min.*

(b) Spectrum of $NH_3.Co^{III}.O_2.Co^{III}.NH_3$ *obtained from oxygenation of CoTSPc (2 ×* 10^{-6} *M) after bubbling* NH_3 *in its aqueous solution.*

In the absence of base, a rapid decay of the spectrum obtained is observed after addition of H_2O_2. This ultimately gave rise to complete decolourization of the solution indicating that an oxidative degradation of the Pc-ring had taken place.

The same, steadily decaying, spectrum (Fig. 9a) could also be obtained through neutralization of a basic CoTSPc/H_2O_2 solution, hence when starting from the suggested Co^{III}TSPc. The striking similarity of the observed spectrum to that of the peroxo bridged adduct, as prepared by oxygenation of CoTSPc under basic conditions (Fig. 9b) gives strong evidence on the nature

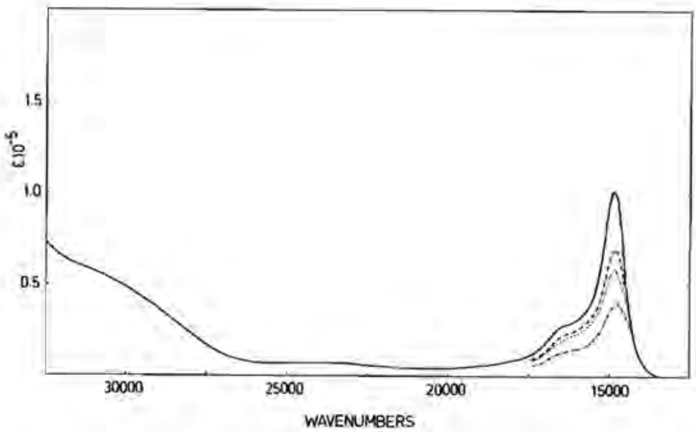


Fig. 10. Product obtained under exclusion of O_2 from the interaction of $Co^{II}TSPc/H_2O_2/ME$ in the absence of base (2×10^{-6} M CoTSPc, 0.1 M ME, 0.06 M H_2O_2). The top of the main peak was recorded with intervals of 10 min.

of the obtained product, *i.e.* $Co^{III}.O_2^{=}.Co^{III}$. This assignment is in accord with observations on the interaction of Co^{III}-cobinamides with H_2O_2 reported by Sigel *et al.* [22]. Kinetic results gave substantial evidence that this interaction gives rise to formation of a μperoxo adduct.

Quite interesting is the behaviour of a CoTSPc solution in the presence of both H_2O_2 and ME under exclusion of oxygen. Under alkaline conditions, the optical spectrum observed is that of the Co^{II}-dimer indicating that Co^{III}TSPc is reduced rapidly. However, under neutral conditions essentially the same spectrum as seen during the steady-state of the catalytic autoxidation reaction was observed. In this case the spectrum suffered decay obviously because of an oxidative degradation by the action of H_2O_2 (Fig. 10). It should be noted that in these experiments no evidence of H_2O_2 decomposition was found.

4. Discussion

Characteristic features of spectra

The optical spectra shown are characterized by a very intensive band in the 15 kK region (*Q* band) together with a shoulder on its high-energy side and a rather broad band in the *N.UV* region (*B* band). Semi-empirical calculations applied by Gouterman and Edwards [23] and Henriksson *et al.* [24] clearly show that these bands can be attributed to allowed phthalocyanine $\pi-\pi^*$ transitions. The broadening of the *B* band is ascribed by Hochstrasser and Marzacco [25] to the presence of underlying $n-\pi^*$ transitions involving the free electrons of the ring nitrogen atoms, an assumption later on confirmed by Gouterman *via* extended Hückel calculations [23]. According to the calculations of Henriksson [24], no significant bands may be expected in the so called "phthalocyanine window" *viz.* 18-25 kK.

Most of our recorded spectra satisfy this prediction more or less, but in the case of Co^{I}TSPc in DMF (Fig. 5) marked bands at 21.2 and 23.2 kK are observable. M.C.D. spectroscopic measurements carried out by Stillman and Thomson [19] revealed that these bands should be ascribed to metal → ligand charge transfer transitions. Similar spectra were obtained by us in aqueous media after chemical reduction by mercaptoethanol (ME), cysteine, or hydrazine. A slight shift of band positions is observed when comparing spectra obtained in DMF and water (Fig. 5 and 6). Considering the well-known tendency of Co^{II}TSPc to form dimers in aqueous solution [8, 15, 16], the observed shift probably is due to dimerization of Co^{I}TSPc in water. Magnetic studies on aqueous solutions of CoTSPc carried out as early as 1964 by Busch *et al.* [26] in fact point in the same direction.

It is noteworthy that only in the presence of base chemical reduction to Co^{I}TSPc occurs, as reflected by the characteristic absorption band in the 22 kK region.

In the absence of base, this band is not observed and only a relatively weak band at ~ 15 kK is shown (Fig. 6), indicating that under these conditions no reduction takes place but merely a complexation. These observations are in accord with similar results reported on comparable complexes. Firstly, Nome and Fendler [27] studied the kinetics of the interaction of cysteine with vitamine B_{12a}. They found that complexation of the Co^{III} complex happened under all pH conditions but its reduction proved to be strongly pH-dependent, to such an extent that in practice no perceptible reduction occurred at pH < 7. Secondly, Wayland and Swartz [28] reported on the interaction of CH_3SH with Fe^{III}myoglobine in an aqueous solution resulting in a stable Fe^{III}/CH_3SH complex in the absence of base. Recuction of the metal centre again occurred only with addition of base (pyridine or imidazole).

Nature of the steady-state intermediate

Steady-state (ss) spectra recorded during the autoxidation of mercapto-ethanol (ME) or cysteine in aqueous media are essentially similar. In addition, comparable spectra are found using DMF as the solvent (in the absence of base). These ss-spectra were compared with spectra associated with different valence states of the cobalt centre or with various oxygenation products obtained in the absence of mercaptan. None of the spectra appeared to be identical with the ss-spectra. On the other hand, utilization of ME in combination with H_2O_2 in a neutral or slightly acidic aqueous solution gave rise to an optical spectrum that is identical with the ss-spectrum.

In order to find out the nature of the complex present during the ss, we will now give a systematic survey of all intermediate complexes which have to be considered as possibly being present during the catalytic reaction. Their optical spectra and ESR features will be compared with the data found for the ss-intermediate. By doing so, it will appear that only the binuclear peroxo adducts have characteristics consistent with those found for the ss-intermediate.

As to the valence state of the ss-intermediate: *Co^{I}*: may be ruled out based on the following observations

- The optical spectrum of Co^{I}TSPc is completely different from the ss-spectrum. The lack of the characteristic absorptions at ~ 22.5 and ~ 14.5 kK in the ss-spectrum means that at best only marginal amounts of Co^{I}TSPc may be present.
- The same ss-spectrum is observed also in the absence of base; it was pointed out that under these conditions the substrate is not able to reduce the Co^{II}-complex.
- The ss-intermediate in DMF is not ESR detectable but under conditions of oxygen depletion the signal of Co^{II}TSPc reappears indicating that in the ss-complex the oxidation state of cobalt is at least two.

Co^{II}: may also be ruled out:

- The ss-intermediate in DMF is not ESR detectable.
- Monomeric Co^{II}TSPc shows a rather intensive band in the *N.UV* region (30.5 kK), whereas the intensity of the corresponding band of the ss-spectrum is appreciably lower.
- Complete dimer formation would account for the absence of an ESR detectable signal but the optical ss-spectra are not in agreement with this assumption. The high intensity of the 15 kK band exhibited both in DMF and H_2O precludes such a dimer of being present in significant amounts.

Co^{III}: A Co^{III}-complex without interaction with coordinated dioxygen is less probable as indicated by the following considerations:

- Oxidation of Co^{III}TSPc by dioxygen normally gives rise to formation of dioxygen adducts, *viz.* $Co^{III}.O_2^{-}$ or $Co^{III}.O_2^{=}Co^{III}$, as was shown in a previous paper [17].
- A comparison of the ss-spectrum with that of electrochemically prepared Co^{III}TSPc in DMF shows noticeable

differences between the band intensities of both the 15 and the 25 kK band.

- $Co^{III}TSPc$ is unstable in the presence of ME/NaOH because of rapid reduction to $Co^{II}TSPc$, as was demonstrated by an experiment in which H_2O_2 was used as oxidizing agent under basic conditions.

The considerations given above show that assignment of the ss-spectra to an oxygen-free cobalt complex is not plausible. Therefore, we will now examine a variety of oxygen adducts possibly formed during the reaction. Complexes that should be considered are the oxygenation products resulting from interaction of $Co^{I}TSPc$ and $Co^{II}TSPc$ with oxygen ($Co^{III}TSPc$ did not react with oxygen).

As to the *oxygenation product of* $Co^{I}TSPc$:

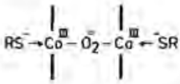
- Oxygenation of electrochemically prepared $Co^{I}TSPc$ gave rise to an optical spectrum shown in Fig. 7. The nature of the product associated with this spectrum is not known. The product did show an ESR signal but poor resolution did not allow further identification. Whatever the identity of this species, its paramagnetic character gives sufficient evidence that it is not the same as that found during the steady-state.
- The observation of the ss-signal also in the absence of base provides another indication that oxygenation products from $Co^{I}TSPc$ can be ruled out. As stated before, under these conditions no reduction of $Co^{II}TSPc$ by ME could be accomplished.

As to the *oxygenation products of* $Co^{II}TSPc$:

- ESR investigation of the frozen ss-solution in DMF gave no evidence of the presence of the 1:1 O_2 adduct at low temperature. Apart from this observation, an 1:1 O_2 adduct if present at low temperature might be expected largely to dissociate into $Co^{II}TSPc$ and O_2 at room temperature, taking into account the low thermodynamic stability of such adducts [29-31]. Hence, we will consider in more detail the binuclear oxygen adduct.

- The optical spectrum of the binuclear oxygen adduct appears to be similar to that found for the ss-intermediate but it is not entirely identical. A comparison with peroxo adducts obtained from the interaction of H_2O_2 with $Co^{II}TSPc$ is helpful. In particular, the changes in the spectra observed with addition of ME in the absence of O_2 appear to be decisive. Thus, in the presence of base, addition of ME to the Co^{III} complex resulted in the formation of $Co^{II}TSPc$. But under neutral conditions, interaction of the intermediate formed (*viz.* $Co^{III}.O_2^{=}.Co^{III}$) with ME immediately gave rise to a spectrum identical with the observed ss-signal. It should be stressed that this phenomenon cannot be attributed to the effect of oxygen presumably liberated by decomposition of H_2O_2. Firstly, no evidence of any gas evolution could be found from sensitive manometric measurements. Secondly, if such a decomposition of H_2O_2 would occur, formation of the ss-signal due to O_2 would be so slow under neutral conditions as to be inconsistent with the rapid formation of the spectrum observed.

We therefore propose on the evidence of the experiments involving H_2O_2 addition that the ss-intermediate is:



$$RS^{-} \rightarrow Co^{III}-O_2^{=}-Co^{III} \leftarrow {}^{-}SR$$

The suggested coordination of the ss-complex by RS^- is made credible from the following indications:

- The optical bands shown at 19 and 24 kK were only observed in the presence of ME.
- According to calculations applied to uncoordinated metal phthalocyanines [23, 24], no optical bands appear in the 18-25 kK region. However upon coordination by

RS^- additional c.t. bands ($RS^- \longrightarrow Co^{III}$) may be expected. Analogous complexes between RS^- and Co^{III} macrocycles are well known in the literature, *e.g.* coordination of vitamin B_{12} by cysteine has been demonstrated to proceed very rapidly giving rise to a stable adduct [27].

Proposed catalytic reaction mechanism

Elucidation of the nature of the ss-intermediate of course is not sufficient to establish the reaction mechanism, but it offers the opportunity to trace a pathway through which the ss-intermediate is being formed. Evidently, such a reaction pathway does not necessarily represent the main route of product formation. The possibility that only a minor part of the cobalt complex is involved in a reaction sequence which is essential for the activity of the catalyst should be considered seriously.

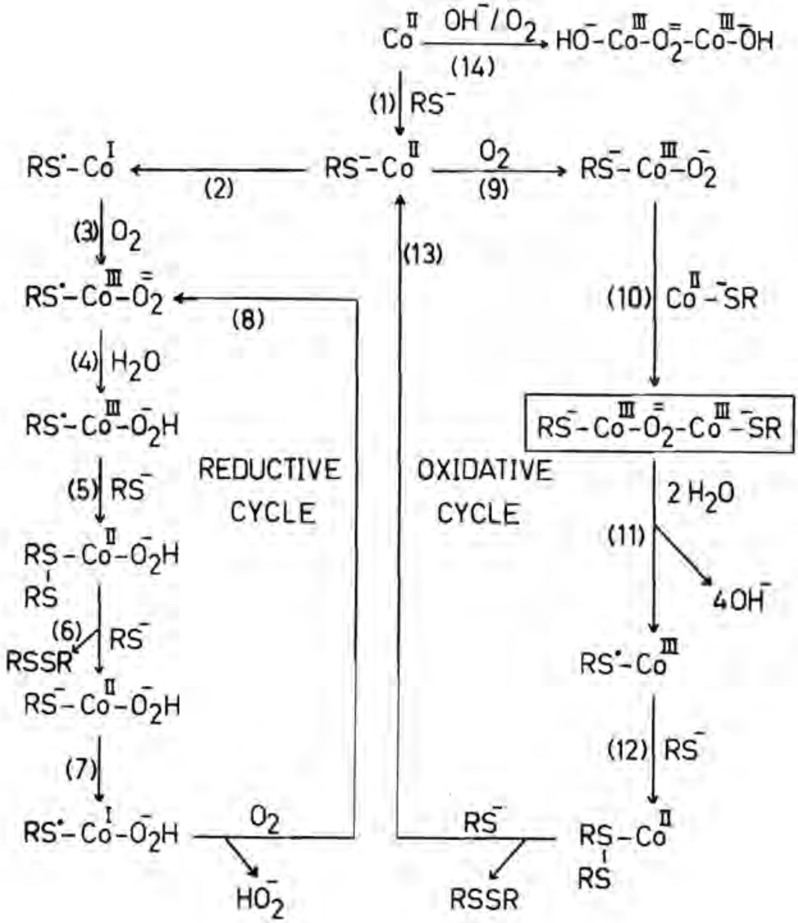
Information that may shed light on this question can be obtained from the kinetics of the catalytic reaction.

1. The observed order with respect to O_2 is negative (~ -0.5). Such a negative order is not easily understood if only one reaction sequence involving the formation of the binuclear peroxo adduct would be operative. The negative order rather points to a reaction model in which oxygen functions as an inhibitor, thus preventing the formation of a highly reactive catalytic species.
2. The remarkable activity exhibited by the reduced catalyst lends support to the suggestion that a catalytic cycle initiated by reduction of the cobalt complex contributes most to the product formation. Otherwise, direct oxygenation of the Co^{II} complex gives rise to formation of the binuclear peroxo adduct being predominantly present during the steady-state of the reaction. The relative stability of this dimeric species accounts for the observed inhibitor function of oxygen.

In view of these facts, we propose a reaction scheme composed of two alternative reaction paths accessible for the reacting cobalt complex referred to as, respectively, the reductive cycle and the oxidative cycle.

<u>Reaction Scheme</u>

(Co is denoting the cobalt phthalocyanine complex)



The important contribution of the reductive cycle in the overall process when oxidizing ME in the presence of base (NaOH/ME = 0.42) may be deduced from the rate dependence on the oxygen pressure (Table 1). It appears that the rate increases about a factor of 2 when reducing $P(O_2)$ from 5 to 1 atm. It should be noted that at least this increase of the rate comes on account of the reductive cycle. Otherwise, an estimate of the contribution of the oxidative cycle would be obtained from experiments carried out at more elevated oxygen pressures. Unfortunately, however, the equipment utilized did not permit application of pressures above 5 atm. Another approach to this question is provided by the experiments carried out in the absence of base. It was demonstrated that under those conditions no reduction of the cobalt complex could be achieved. So the (low) activity measured in the absence of base (*see* Fig. 1) may originate from the oxidative cycle. At this stage, no quantitative data on its contribution in the presence of base are available due to lack of information on the kinetic effect of RS^- in this cycle. However, a relatively large contribution of the oxidative cycle is supposed when using low amounts of base (*e.g.*, NaOH/ME = 0.035) as inferred from the 0^{th} order with respect to O_2 observed in that case. Such a kinetic behaviour is expected for the oxidative cycle as the accumulation of the dimeric peroxo adduct suggests its reductive decomposition to be the rate determining step (reaction (11)).

As noted before, the contribution of the reductive cycle in the oxidation process is more significant at higher base content. But also in that case only a low fraction of the total amount of cobalt complex would be operative in the reductive cycle, as derived from the results on the effect of partial reduction of the catalyst. The extremely efficient reductive cycle is initiated by a reduction step involving the formation of $Co^{I}TSPc$ (reaction (2)). The subsequent interaction

with oxygen is assumed to give rise to formation of the oxygen adduct of the Co^{I} complex. A Co^{I}/Co^{II} reoxidation step as suggested by Kundo and Keier [3] is less probable regarding the following observations.
1. Neither ESR nor optical spectroscopy gave evidence of formation of $Co^{II}TSPc$ as a product from oxidation of $Co^{I}TSPc$ by oxygen.
2. Oxidation of a macrocyclic $Co^{I}N_4$ complex by oxygen was shown by Simic and Hoffman [20] to lead to the same product as obtained from the interaction of $Co^{II}N_4$ with O_2^{-}. Although the identity of the product was not clear, conclusive evidence was found that no Co^{I} or Co^{III} complex was formed, thus ruling out a simple electron transfer reaction and establishing the formation of an oxygen adduct. Hence in the reaction scheme, oxygen adduct formation with a concomitant two-electron transfer seems more plausible (reaction (3)). The oxygenation reaction is probably a rapid one as may be deduced from kinetic data reported on oxygenation of similar macrocyclic complexes ($k = 1.7 \times 10^{9}\ M^{-1}.S^{-1}$) [32].

The disulfide formation is assumed to proceed in the coordination sphere of the Co^{III}-peroxo complex. A mechanism involving the production of free $RS^{\cdot}$ radicals seems less probable taking into account the high selectivity of the oxidation process which produces exclusively RSSR. This would not be expected if free $RS^{\cdot}$ radicals were generated regarding the extremely rapid reaction of $RS^{\cdot}$ with O_2 ($k = 2 \times 10^{9}\ m^{-1}.S^{-1}$) [33] producing such species as $RSO^{\cdot}$ and $RSO_2^{\cdot}$ [34]. On the other hand, product formation through interaction of free RS^{-} with *coordinated* $RS^{\cdot}$ and subsequent electron transfer within the complex is quite probable regarding the high reaction rate of free $RS^{\cdot}$ with RS^{-} ($k = 2.4 \times 10^{9}\ M^{-1}.S^{-1}$) resulting in the formation of $RSSR^{\dot{-}}$ radicals [35].

The production of H_2O_2 as proposed in the reductive cycle is derived from experiments using soluble polymeric amines as basic agent [12]. In those experiments H_2O_2 accumulation was observed, but the level appeared to be strongly dependent on the amount of additional base (NaOH) and no perceptible H_2O_2 accumulation occurred when more than 1 mmole of NaOH per ml ME was used. This phenomenon was ascribed to a rapid reaction of H_2O_2 with ME, the latter being confirmed by our present measurements. Therefore, the absence of a detectable amount of H_2O_2 in the reaction solution does not preclude its intermediate production as suggested in reaction (8). Expel of H_2O_2 from the Co^I complex and substitution by O_2 is facilitated by a weakening of axial bonding arising from a shift towards square planar geometry, which may be expected for metal complexes with a d^8 configuration.

As to the rate determining step within the reductive cycle, no conclusive evidence is obtained at this moment. But from the observed rate dependence on the amount of substrate, obeying Michaelis Menten kinetics, we tentatively suggest it to be reaction (5) or (6). The high activity of the reductive cycle may be explained from the feasibility of a two-electron transfer within the Co^IO_2 complex. Hence, the conversion into a thermodynamically favourable peroxo adduct is effected without formation of the relatively inert dimeric μ-peroxo complex, which does occur in the oxidative cycle (reaction (10)).

The activity of the catalytic system as a function of the amount of base used has been shown to pass through a maximum (Fig. 1). The initial rise of activity with increasing amounts of NaOH generating RS^-, may be understood from the enhanced reduction power of the substrate, thus favouring reaction (2) and giving rise to a larger contribution of the reductive cycle. But an explanation of the fall in activity as observed for pH values above 10 is less obvious. A similar rate dependence was reported by Wagnerová *et al.* [4] for the autoxidation of cysteine catalyzed by CoTSPc. They explained the observed maximum at pH = 9.7 in terms of the various dissociation equilibria in which cysteine is involved. Assuming the zwitterion to be the most reactive form of the substrate, a satisfying fit with the experimentally observed maximum was obtained. However, such an explanation does not hold in case ME is used as the substrate. We therefore suggest for the fall in activity observed at higher pH values as to originate from a deactivation process of the catalyst itself. Taking into account the tendency of CoTSPc to form binuclear oxygen adducts arising from axial coordination of OH^-, its rate being strongly dependent on the pH [9], the deactivation of the catalyst is attributed to the formation of such oxygen bridged dimers (reaction (14)).

The proposed reaction scheme accounts for the correlation found by Kundo and Keier [6] between catalytic activity and reducibility of the catalyst. The reaction mechanism suggested by these authors, involving a Co^{II}/Co^{I} redox mechanism, however, ignores the ability of the catalyst to form oxygen adducts. And this ability appears to be essential for catalytic activity according to findings reported by Wagnerová *et al.* [4, 5]. These authors suggest the reactive intermediate to be a mononuclear oxygen adduct. The mechanism presented by us endorses this view but distinguishes the important role of reduction prior to formation of the oxygen adduct. In that case, oxygenation is connected with the formation of a reactive mononuclear peroxo adduct (reaction (3)). Without such a reduction taking place, oxygenation involves the formation of an unstable superoxo complex stabilizing itself by dimerization into a relatively inert peroxo complex (reaction (10)). The elucidation of this reaction path points to a possibility to improve catalytic activity appreciably. Thus, restrictions imposed on the catalyst towards dimerization into peroxo bridged complexes will give rise to a larger contribution of the reductive cycle, resulting in a higher activity. And this is confirmed by our results on the activity of polymer attached cobalt phthalocyanines [11, 12, 36].

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CHAPTER 7

FINAL DISCUSSION

1. Summary of the results

Investigations on polymer attached cobalt phthalocyanines used as catalysts for the autoxidation of mercapto-ethanol (ME) have led to some remarkable results, the most pronounced of which being summarized now.

Monofunctional catalysts

Cobalt(II)-tetramino-phthalocyanine ($CoPc(NH_2)_4$) was covalently bonded through its ring substituents onto a cross-linked poly (acrylamide) carrier (Enzacryl AA). Application of the water-swellable polymer complex as the catalyst in the presence of NaOH led to the following observations:

- No deactivation of the catalyst is observed under reaction conditions, its catalytic activity being essentially the same in subsequent runs.
- The activity of the polymeric system exceeds that of a water-soluble and polymer-free catalyst, *i.e.* cobalt-tetrasulfo-phthalocyanine (CoTSPc), by about a factor 6. This observation is the more remarkable as for the polymeric system the rate is strongly dependent on particle size and, therefore, must be diffusion controlled.

Examination of the Enzacryl attached catalyst by ESR spectroscopy has revealed the following:

- A significant part of the cobalt complexes is present in the form of mononuclear species, in particular under reaction conditions, *i.e.* in the swollen state of the polymer matrix.

- An effective separation between the mononuclear species, due to the polymer matrix, is also maintained under conditions usually favouring the formation of dioxygen bridged dimers.

Bifunctional catalysts

As stated in the introduction of this thesis, one of our aims is to develop a bifunctional catalyst, *i.e.* a system possessing both basic sites and oxidation sites in cooperative interaction. In view of this, polymers (or inorganic matrices) with incorporated amine groups were used as the carrier of cobalt-phthalocyanine. Two different types of catalyst could be obtained depending on the way of coupling the cobalt complex onto the carrier. In the first type, attachment was accomplished by complexation, arising from a coordinative interaction between polymer bound NH_2 groups and the cobalt centre. Conclusive evidence of this so called axial coordination was obtained from ESR spectra recorded on the catalyst complex, showing the characteristic ^{14}N triplet splitting on the Co^{II}-signal. However, dipolar interactions between phthalocyanine ring substituents (*e.g.* COO^- or SO_3^-) and amine groups of the carrier may also contribute to the binding. In the second type of catalyst, binding occurred through a peptide linkage between an amine group of the polymer and a carboxy group of a tetracarboxy-phthalocyanine ($CoPc(COOH)_4$). Under catalytic conditions, however, also a coordinative bonding between polymeric ligands and the cobalt centre is to be expected.

Application of these catalysts has led to the following interesting results:

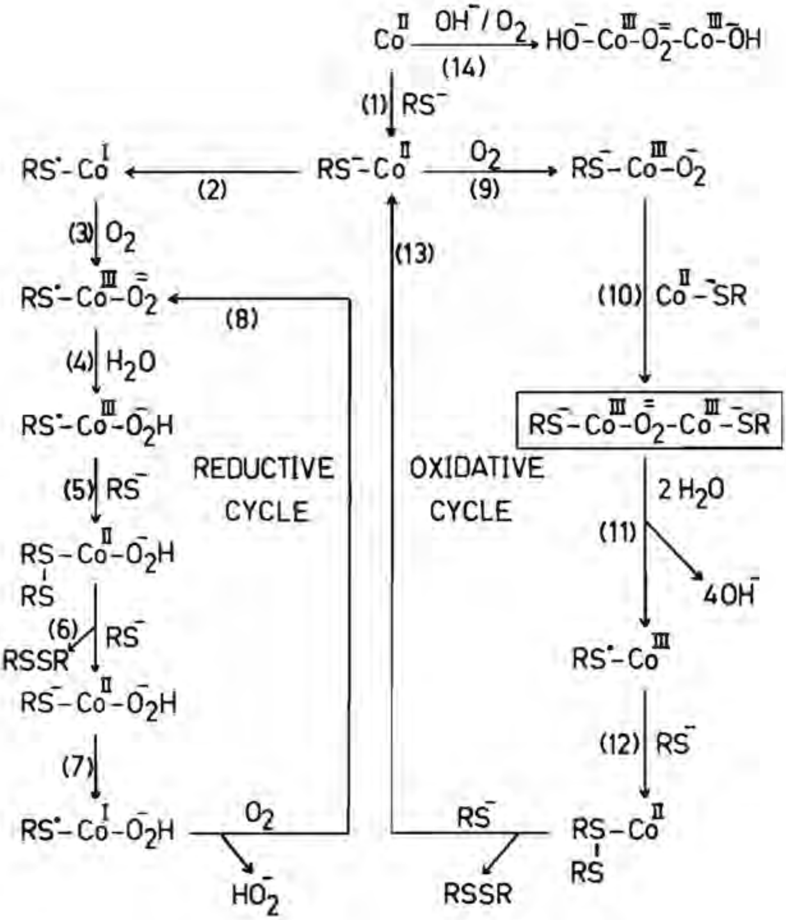
- The catalytic systems obtained have proved to be bifunctional as no additional base is required for activity.
- In particular for the bifunctional systems soluble in

water, a significant enhancement of specific activity is observed compared with the conventional NaOH/CoTSPc system (about a factor 50).

- The extremely high activity is accomplished with a relatively low number of basic groups incorporated in the polymer. This observation indicates a remarkably effective cooperation between basic sites and oxidation sites within the catalytically active complex.
- The polymeric character of the base appears to be essential for the activity of the catalyst.
- In the absence of additional base a steady loss of activity of the catalyst is observed, which is attributed to the formation of traces of strong sulfurcontaining oxo-acids, poisoning the basic sites of the catalyst.
- This poisoning may be prevented by adding low amounts of alkaline base to neutralize these acids. But in some cases, NaOH addition gave rise to a complete loss of activity caused by a base-induced decomplexation of the polymer/CoPc complex. However, when using polymers with a high density of basic groups *e.g.* poly(vinylamine), such a deactivation by decomplexation was not observed and as anticipated, activity was maintained during a longer period of reaction. As might be expected, the most stable catalyst was obtained after covalent coupling of the cobalt complex, through a peptide linkage between its Pc-ring and the polymer. When progressively adding higher amounts of NaOH to the latter catalyst, a loss of activity is still observed. However, this effect is ascribed to a decrease of the local substrate concentration within the polymer coil, which is governed by the pH of the solution, rather than to decomplexation.
- The bifunctional catalysts may also be applied in non-aqueous media, provided that small amounts of water (*e.g.* 1% V/V) are present. The essential role of water is assumed to be that of a mediator for

proton transfer to the $O_2^{=}$ moiety of the intermediate formed $RS^{\bullet}\text{-}Co^{III}\text{-}O_2^{=}$ (*c.f.* Scheme 1, reaction (4)).

Scheme 1

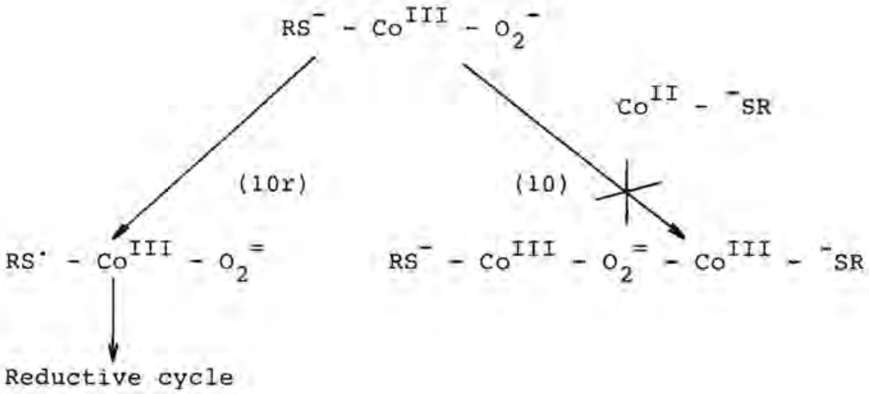


2. Mechanistic interpretation of the observed phenomena

Investigations on the mechanism of the conventional (polymer-free) NaOH/CoPc system have led to a suggested reaction model consisting of two parallel reaction paths accessible for the cobalt complex. One of which, involving oxygenation of the Co^{II}-complex (reaction (9)), leads to the formation of a relatively inert dimeric peroxo adduct. According to optical measurements, the major amount of cobalt complex present during the steady-state is represented by this species. On the other hand, as suggested by kinetic measurements, reduction of the cobalt(II)-complex (reaction (2)) gives rise to initiation of an extremely active catalytic cycle, the so called reductive cycle. We could demonstrate that the activity of the catalytic system is predominantly originating from this cycle which, however, usually contains only a small fraction of the total amount of cobalt complex.

The proposed mechanism accounts for the higher activity observed for the polymer attached catalyst where a cross-linked poly(acrylamide) (Enzacryl AA) was used as the carrier. In that case, oxygen bridged dimers are not easily formed due to restrictions imposed by the polymer matrix. This will give rise to a larger contribution of the reductive cycle resulting in a higher specific activity (activity per mole of catalyst). The shift within the mechanism towards the reductive cycle is probably mediated by the complex $RS^- - Co^{III} - O_2^-$ which is produced *via* reaction step (9). An alternative for reaction (10), leading to the binuclear peroxo adduct, is offered by an internal electron transfer as depicted in Scheme 2:

Scheme 2



It will be obvious that the resulting peroxo adduct is the same as that appearing from oxygenation of the reduced catalyst.

A similar mechanistic approach is also suitable for the bifunctional catalysts which use water-soluble polymeric bases as a carrier. In those cases, dimerization is hindered largely because of a shielding effect exerted by the polymer coils, each containing no more than one molecule of cobalt complex. Another effect attained by the use of a polymeric base is the increased local concentration of basic groups, due to a distribution in separate coils which is a characteristic feature of diluted polymer solutions. The localization of bound RS^- within these coils will probably contribute appreciably to the excellent catalytic activity exhibited by the bifunctional catalysts. This assumption involves that a decrease of the local RS^- concentration would give rise to a reduced catalytic activity. And this was indeed the case, *i.e.* the expel of bound RS^- from the polymer coils - due to an increase of the pH by NaOH addition - resulted in a reduction of the catalytic activity of the peptide bonded complex. In the present study, we did not examine the influence of the chemical behaviour of the base (as *e.g.* pK_a value or its donor ability). Preliminary experiments* indicate that these parameters may also be of interest.

3. Some considerations on the unique properties of cobalt-phthalocyanine as a catalyst for the autoxidation of mercaptans

As was shown earlier, reduction of the cobalt(II) complex resulting in Co^{I}TSPc is a prerequisite for an extraordinarily active catalytic cycle. The high activity obtained in that case may be explained from the feasibility of a two-electron transfer involving the redox couples Co^{I}/Co^{III} and $O_2/O_2^{=}$, hence producing a thermodynamically favoured peroxo complex ($Co^{III} - O_2^{=}$). An efficient catalytic cycle is therefore strongly related to the ability of the metal centre to allow such a two-electron transfer and to form an adduct with oxygen. But according to literature data [1], the reducibility of the cobalt(II) ion is responsive to the extent and type of unsaturation present in the cyclic ligand. Thus, progressive amounts of ligand unsaturation increase the reducibility of the Co^{II} complex. This effect was ascribed to a considerable amount of in-plane ligand character of the lowest

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*The amount of a low molecular amine, *i.e.* bis-(aminopropyl)-amine (BAA), required to reach an appropriate catalytic activity is lower than that of NaOH (use of 0.5 mmole of BAA per ml of ME led to a specif. activ. of 76 ml O_2/min.µmole cat.)

unoccupied molecular orbital pertaining to the d^8 (Co^I) metal complex. It may therefore be expected that the required reduction process of the cobalt ion is appreciably facilitated by the conjugated system of the phthalocyanine ligand. On the other hand, axial coordination of strong donors as RS^- or $RS^\cdot$ will favour oxygenation with concomitant oxidation to Co^{III}.

In view of these considerations it may be expected that relatively favourable conditions are provided for a Co^I/Co^{III} couple due to the combined effect of the phthalocyanine ring and the axial coordination of RS^- or $RS^\cdot$. However, as pointed out in this thesis, such a couple will be operative to a high degree only if formation of a binuclear peroxo adduct is avoided.

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SUMMARY

This thesis reports on an investigation of polymer attached cobalt-phthalocyanines (CoPc) applied as catalysts in the oxidation of mercapto-ethanol to the disulfide by oxygen in aqueous media.

Attention was given to the kinetic effects of heterogenizing the catalyst by attachment to a cross-linked poly(acrylamide) carrier. It was found that the polymer attached catalyst, coupled *via* its NH_2 ring-substituent onto the polymer by means of cyanuric chloride, was appreciably more active than its homogeneous counterpart (about a factor 6, chapter 3I) Characterization of the polymeric catalyst by ESR spectroscopy revealed that at least part of the catalyst is present as mononuclear complexes. Yet, more important with respect to the catalytic activity is the observation that the formation of oxygen bridged dimers is severely hindered by the polymer matrix (chapter 3II). The relevance of the latter feature becomes apparent from an investigation on the mechanism of the autoxidation of mercapto-ethanol, catalyzed by a conventional water-soluble cobalt(II)-phthalocyanine catalyst.

Investigations on the mechanism of the NaOH/CoPc system (chapter 6) have led to a suggested reaction model consisting of two parallel reaction paths accessible to the cobalt complex. One of these, the so-called oxidative cycle, involves a direct oxygenation of the Co^{II}-complex leading to the formation of a relatively inert dimeric peroxo adduct, which is the species predominantly being present during the steady-state of the reaction. The contribution of this cycle in the overall rate, however, is low. The other pathway, the reductive cycle, accounting for the major product formation involves a $Co^{II} \rightarrow Co^{I}$ reduction step prior to oxygenation and internal electron transfer. The picture emerging from this reaction model shows that in fact the rate of oxidation is generated by only a

low fraction of cobalt complex, while the main part is accumulated in a dimeric peroxo adduct, thus functioning as a sink for the catalyst. As expected, polymer attachment of the catalyst, resulting in hindrance of peroxo adduct formation, appreciably enhanced the activity.

A further aim of this thesis is to prepare and investigate a bifunctional catalyst, *i.e.* a polymer attached system not only furnishing the oxidation catalyst but also the basic groups which are required in the oxidation process. In view of this, soluble polymers carrying amine groups were used *e.g.* poly(vinylamine), poly(ethylenimine), and poly(acrylamide) with incorporated basic NH_2 groups. Two different types of catalysts were obtained depending on the way of coupling the cobalt complex onto the carrier. In the first type attachment was accomplished by complexation arising from a coordinative interaction between the polymer bound NH_2 groups and the cobalt centre. In the second type, binding was established through a peptide linkage between a carboxy substituent of the phthalocyanine ring and a polymeric amine group. It was shown that within the catalytic systems thus obtained a remarkably effective cooperation between basic sites and oxidation sites occurred (chapter 4 and 5). This could be derived from the excellent catalytic activity exhibited by the polymeric catalysts in the absence of additional base. Thus, compared with the conventional NaOH/CoPc system an enhancement in activity per cobalt site by about a factor of 50 was noted. In addition, the high activity was achieved with a relatively low number of basic groups as supplied by the polymer.

Two main reasons, both inherently connected with the polymeric character of the base, can account for the high activity of the bifunctional polymeric systems (chapter 4). Firstly, dimerization of the cobalt complexes is hindered largely because of a *shielding* effect exerted by the polymer coils, which under usual conditions contain no more than one catalytic unit per coil. Owing to the coordinative interaction of polymer bound RS^- with the cobalt centre, the catalyst is expected to be surrounded by polymer segments. Secondly, as a consequence of the specific character of a very dilute polymer solution (approx. 0.1g/l) which consists of spatially distributed coils in the solvent, aggregates of high base density are formed when using polymers carrying basic groups. The accumulation of bound RS^- in the coils, therefore, will appreciably *increase the local* RS^- *concentration* in the environment of the catalyst. In accordance with the proposed kinetics of the reaction, this effect appeared to give rise to an enhanced rate of oxidation.

It was demonstrated that the polymeric catalysts can also be applied in toluene provided that a small amount of water is present, probably required to afford a suitable proton transfer medium (chapter 5). This observation offers an opportunity towards a more simple removal of mercaptan sulfur compounds from cracked gasolines, avoiding the usually applied two-phase process.

In the absence of additional NaOH, a deactivation of the catalyst was observed during the course of the reaction, which is ascribed to a poisoning of the basic sites due to low amounts of acidic by-products. Addition of NaOH to neutralize these acids and to prevent poisoning in some cases led to rupture of the polymer/CoPc complex (chapter 4). But employment of a strongly complexing polymer, *i.e.* poly(vinylamine), in particular when catalyst coupling was established through a peptide linkage, improved the stability of the polymeric catalyst appreciably. In that case, *in situ* removal of acids was possible (by addition of NaOH) without concomitant rupture of the active polymer/CoPc complex (chapter 5).

SAMENVATTING

In dit proefschrift wordt een onderzoek beschreven naar de katalytische eigenschappen van aan polymeer gehechte cobalt-phthalocyanines (CoPc) in de oxidatie van mercapto-ethanol tot disulfide i.a.v. zuurstof, uitgevoerd in waterige media.

De kinetische effecten van het heterogeniseren van de katalysator, door binding aan een cross-linked poly(acrylamide) drager, werden onderzocht. Gevonden werd dat het polymeer/katalysator complex, gekoppeld via een NH_2-ringsubstituent m.b.v. trichloro-triazine, aanzienlijk aktiever is dan de vrije katalysator (~ factor 6, hst. 3I). Karakterisering van de polymere katalysator d.m.v. ESR spectroscopie bracht aan het licht dat tenminste een gedeelte van de katalysator aanwezig is in de vorm van mononucleaire complexen. Belangrijker nog m.b.t. de katalytische aktiviteit, is de waarneming dat de vorming van dimere zuurstofadducten ernstig wordt gehinderd door de polymere matrix (hst. 3II). Het essentiële belang hiervan blijkt uit de resultaten van een onderzoek naar het mechanisme van de autoxidatie van mercapto-ethanol, gekatalyseerd door een conventionele water-oplosbare cobalt(II)-phthalocyanine.

Mechanistisch onderzoek van het NaOH/CoPc-systeem (hst. 6) heeft geleid tot een gesuggereerd reactiemodel bestaande uit twee parallele reaktiewegen. Een ervan representeert de zgn. oxidatieve cyclus, waarin een direkte oxygenering van het Co^{II} complex leidt tot de vorming van een relatief inert dimeer, nl. een peroxo-adduct. Het is gebleken dat dit complex overwegend aanwezig is tijdens het verloop van de oxidatie. De effectieve bijdrage van de oxidatieve cyclus in de gemeten snelheid is echter laag. De andere reaktieweg, de zgn. reduktieve cyclus, welke in sterke mate de snelheid van produktvorming bepaalt, wordt ingeleid door een $Co^{II} \rightarrow Co^{I}$ reduktiestap, waarna oxygenering en een interne electronenverhuizing plaatsvindt. Het beeld dat uit dit reaktiemodel naar voren komt, laat zien dat slechts een gering gedeelte van het cobalt complex werkelijk effectief benut wordt tijdens het oxidatieproces, terwijl de meerderheid wordt opgeslagen in de vorm van het dimere peroxo-adduct dat als een val voor de katalysator functioneert. Zoals verwacht mocht worden, blijkt een aanzienlijke aktiviteitsverhoging realiseerbaar door hechting van de katalysator aan een polymeermatrix, waardoor de vorming van genoemde dimere peroxo-adducten belemmerd wordt.

Een ander oogmerk van dit proefschrift is de bereiding en bestudering van een bifunctionele katalysator, d.w.z. een polymeer systeem dat niet alleen de oxidatiekatalysator bevat, doch ook de basische groepen levert welke noodzakelijk zijn in het oxidatieproces. Met het oog hierop werd gebruik gemaakt van water-oplosbare polymeren die aminogroepen bevatten t.w. poly(vinylamine), poly(ethyleenimine) en poly(acrylamide) waarin basische NH_2-groepen aangebracht zijn. Twee verschillende katalysatortypen werden verkregen afhankelijk van de wijze van koppeling met de drager. In het eerste type werd de hechting tot stand gebracht door complexering als gevolg van een coordinatieve interactie tussen polymeergebonden NH_2-groepen en het cobaltion. In het tweede type werd koppeling bereikt via een peptide-brug tussen een carboxyl-substituent van de Pc-ring en een polymere NH_2-groep. Aangetoond kan worden dat er voor de zo verkregen katalytische systemen sprake is van een opmerkelijk effectieve samenwerking tussen de basische groepen en de oxidatie-katalysator (hst. 4 en 5). Dit kon worden afgeleid uit de voortreffelijke katalytische aktiviteit van de polymere katalysatoren in afwezigheid van extra toegevoegde NaOH; d.w.z. vergeleken met het conventionele NaOH/CoPc-systeem werd per cobaltion een aktiviteitsverhoging van ca. een faktor 50 gekonstateerd. Daarenboven werd deze hoge aktiviteit bereikt met een relatief geringe hoeveelheid basische groepen, geleverd door het polymeer. Twee hoofdredenen, beide inherent gerelateerd aan het polymere karakter van de base, zijn aansprakelijk voor de hoge aktiviteit van de bifunctionele polymere systemen (hst. 4). Ten eerste wordt dimerisatie van de cobalt-complexen in belangrijke mate verhinderd door een afschermingseffect uitgeoefend door de polymere kluwens, welke onder de gebruikelijke omstandigheden hoogstens één katalytische eenheid bevatten. Op grond van de coordinatieve interactie van polymeergebonden RS^- met het cobaltion kan nl. worden verwacht dat de katalysator wordt omringd door polymeersegmenten. Ten tweede worden aggregaten van een hoge basedichtheid gevormd bij toepassing van basische polymeren, als gevolg van het specifieke karakter van verdunde polymeeroplossingen (nl. ruimtelijk verdeelde kluwens in het oplosmiddel). De opeenhoping van gebonden RS^- in deze kluwens heeft een aanzienlijke verhoging van de locale RS^- concentratie in de direkte omgeving van de katalysator tot gevolg. In overeenstemming met de kinetiek van de reaktie bleek dit te leiden tot een verhoogde oxidatiesnelheid.

De polymere katalysatoren blijken ook toepasbaar in tolueen op voorwaarde dat een geringe hoeveelheid water aanwezig is, dat waarschijnlijk dient als medium voor protontransport (hst. 5). Dit opent de mogelijkheid tot een vereenvoudigde procesvoering t.a.v. de verwijdering van mercaptaan uit oliefracties doordat het gewoonlijk toegepaste twee-fase proces nu kan worden vermeden.

In de afwezigheid van extra NaOH trad deactivering van de katalysator tijdens het verloop van de reaktie op, toegeschreven aan vergiftiging van de basische plaatsen door geringe hoeveelheden zure bijprodukten. Toevoeging van NaOH om deze zuren te neutraliseren en de vergiftiging te voorkomen, leidde in sommige gevallen tot verbreking van het polymeer/CoPc-complex (hst. 4). Maar gebruik van een sterk complexerend polymeer zoals poly(vinylamine), vooral bij peptide-koppeling, verbeterde de stabiliteit van de polymere katalysator aanzienlijk. In dat geval bleek *in situ* verwijdering van zuren mogelijk (door toevoeging van NaOH) zonder optredende afbraak van het aktieve polymeer/CoPc-complex (hst. 5).

LEVENSBERICHT

De schrijver van dit proefschrift werd geboren op 25 oktober 1942 te Velsen. Vanaf 1955 tot 1960 werd de Rijks-H.B.S. aldaar doorlopen. Na het behalen van het H.B.S.-B. diploma verhuisde hij naar Limburg en trad in dienst van de Staatsmijnen (DSM).
Nadat het diploma chemisch analist was behaald, werd hij tewerkgesteld bij de groep polymeerchemie. Gedurende de periode dat hij daar werkzaam was, behaalde hij via een schriftelijke cursus (P.B.N.A.) het diploma Chemisch Technicus.

In 1969 werd gestart met de studie aan de T.H. Eindhoven, welke in oktober 1973 in de vakgroep Katalyse werd afgerond. In februari 1974 kwam hij in dienst van dezelfde vakgroep en werd gestart met het onderzoek dat geleid heeft tot dit proefschrift. Daarnaast heeft hij zich beziggehouden met het onderzoek naar het mechanisme van de autoxidatie van cysteine, gekatalyseerd door Cu^{II}-ionen.

Per 1 augustus 1978 is hij in dienst getreden van het Sophianum College te Vaals als leraar wiskunde/scheikunde.

Stellingen behorende bij het proefschrift van

J. Zwart

15 september 1978

STELLINGEN

1. Een Cu^{II}/Cu^{I} redoxmechanisme, zoals voorgesteld voor de door koperionen gekatalyseerde autoxidatie van thiolen, is aan ernstige bedenkingen onderhevig.

   (1) T.J. Wallace, A. Schriesheim, H. Hurwitz and M.B. Glaser, Ind. Eng. Chem. Process Des. Develop., 3 (1964) 237.

   (2) C.S. Swan and D.L. Trimm, J. Appl. Chem., 18 (1968) 340.

2. De thermodynamische verklaring, gegeven door Kundo *et al.* voor het bij de oxidatie van ethaanthiol als funktie van de pH waargenomen aktiviteitsoptimum, suggereert ten onrechte dat een dergelijk aktiviteitsprofiel kenmerkend is voor de oxidatie van thiolen.

   G.I. Leschchinskaite, N.N. Kundo and V.G. Chervova, J. Appl. Chem. (USSR), 50 (1977) 124.

3. De veronderstelling van Wagnerová *et al.* dat tijdens de oxidatie van hydroxylamine, gekatalyseerd door cobalt-phthalocyanine, wel het mononucleaire zuurstofadduct van het cobalt-komplex gevormd wordt, doch niet tegelijkertijd het binucleaire zuurstofadduct, is in strijd met de door deze auteurs gevonden kinetiek van de oxygenering van cobalt-phthalocyanine.

   (1) D.M. Wagnerová, E. Schwertnerová and J. Veprek-Siska, Collection Czech. Chem. Commun., 39 (1974) 3036.

   (2) D.M. Wagnerová E. Schwertnerová and J. Veprek-Siska, Collection Czech. Chem. Commun., 39 (1974) 1980.

4. Bij het door Jameson en Blackburn geponeerde mechanisme van de autoxidatie van ascorbinezuur, gekatalyseerd door koperionen, vindt de verwaarlozing van de relatieve hoeveelheid koperdimeer, aanwezig onder reaktiekondities, geen rechtvaardiging in de numerieke waarde van de dimerisatiekonstante.

   R.F. Jameson and N.J. Blackburn, J.C.S. Dalton, (1976) 534.

5. Indien tijdens autoxidatie-experimenten in de vloeistoffase de hoeveelheid katalysator ongelimiteerd hoog wordt opgevoerd en de vertekening van de waargenomen verschijnselen tengevolge van ernstige diffusielimitering van zuurstof niet wordt onderkend, bestaat het gevaar dat slechts een karikatuur verkregen wordt van hetgeen men beoogt.

   D.J. Cookson, T.D. Smith, J.F. Boas, P.R. Hicks and J.R. Pilbrow, J.C.S. Dalton, 109 (1977).

6. Terroristische akties krijgen, in verhouding tot het aantal slachtoffers dan wel de politieke en materiële effekten ervan, onevenredig veel aandacht van de media.

   Daar één van de oogmerken van dergelijke akties veelal is het verkrijgen van een maximale publiciteit, verdient het aanbeveling de nieuwswaarde ervan tot zijn ware proporties terug te brengen.

7. Een wapen dat de vrede werkelijk kan dienen is een wapen tegen de wapenwedloop.

   S.I.P.R.I. Jaarboek, Stockholm 1978.

8. In geval van verplichte deelneming van zowel mannelijke als vrouwelijke werknemers in een pensioenfonds, dienen de daaruit voortkomende rechten t.a.v. het weduwnaarspensioen gelijkwaardig te zijn aan die van het weduwepensioen.

9. Spier- en denkarbeid dienen uitgesloten te worden van de slogan: 'Wees zuinig met energie'.

10. Het teruglopen van het aantal leerlingen in het Middelbaar Onderwijs leidt tot een sterker accent op de werving ervan. Een gevaarlijk middel daartoe is echter versoepeling van de aan de leerling te stellen eisen, daar dit diploma-inflatie tot gevolg zal hebben.

11. Bij de beslissing omtrent het al of niet doorvoeren van studentenstops dient de maatschappelijke behoefte aan afgestudeerden leidraad te zijn.

12. Het is tekenend voor onze Westerse arbeidsethos, dat een geringe vermindering van de vraag naar arbeid gezien wordt als een groot sociaal probleem. Een oplossing die genoemd wordt is herverdeling van de arbeid. Het ware beter een herverdeling van de vrije tijd te overwegen.

13. Wie zijn hond in andermans tuin uitlaat, gaat de perken te buiten.