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Polymeric Schiff's Base Chelates and Their Precursors

6[a] Covalently Polymer Bound Cobalt Chelates from Divinylsalenes and Their Dioxygen Binding and Catalytic Activity

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SUMMARY

Various divinyl-Schiff's base ligands 3 were synthesized from 2-hydroxy-5-vinylbenzaldehyde (2) and diamines. Copolymerization of 3 with styrene directly leads to covalently polymer bound ligands 4. Introduction of Co(II) resulted in the formation of the chelates 6. Covalently polymer bound chelates show high activity for the reversible binding of dioxygen under formation of mononuclear superoxo complexes. The chelates exhibit good activities for the oxidation of 2,6-di-tert-butylphenol (9).

INTRODUCTION

As mentioned in the preceding paper (Ref. 1) low molecular Schiff's base chelates as Co(salen) 1a and Cosaldpt 1b exhibit excellent properties for binding of small molecules and catalytic activities. In order to profit from polymer binding various covalently polymer bound Schiff's base chelates were synthesized by us (Ref. 2-5). The present work describes an easy three step synthesis of such chelates starting from 2-hydroxy-5-vinylbenzaldehyde (2). The obtained divinyl compounds 3 were used for copolymerization with styrene in order to get after Co(II) introduction, unsoluble polychelates 6 directly. The unsoluble catalyst beds were examined for dioxygen binding and as catalysts for the oxidation of a phenol (s. also Ref. 6).

RESULTS AND DISCUSSION

In Ref. 1 we described a possibility for obtaining covalently polymer bound Schiff's base chelates by direct copolymerization of protected 2 with styrene followed by some polymer analogous reactions. The second possibility of receiving polymer bound chelates starting from 2 is the reaction of this monomer with varying diamine compounds leading to divinyl ligands 3a-d (Scheme 1). 3a-d were synthesized in good yields from 2 and diamines in ethanol. Bridge variations lead to steric and electronic differences within the ligands (Ref. 7-10), so that by varying the bridge, polymer bound chelates with different properties in respect to some catalysis reactions and oxygen uptake can be expected. The soluble compounds 4a-e (reaction time 2 h) as well as the gel like polymers 4f-l (reaction time 168 h) are obtained by radical polymerization of the monomers 3a-d with styrene in solution (Tab. 1).

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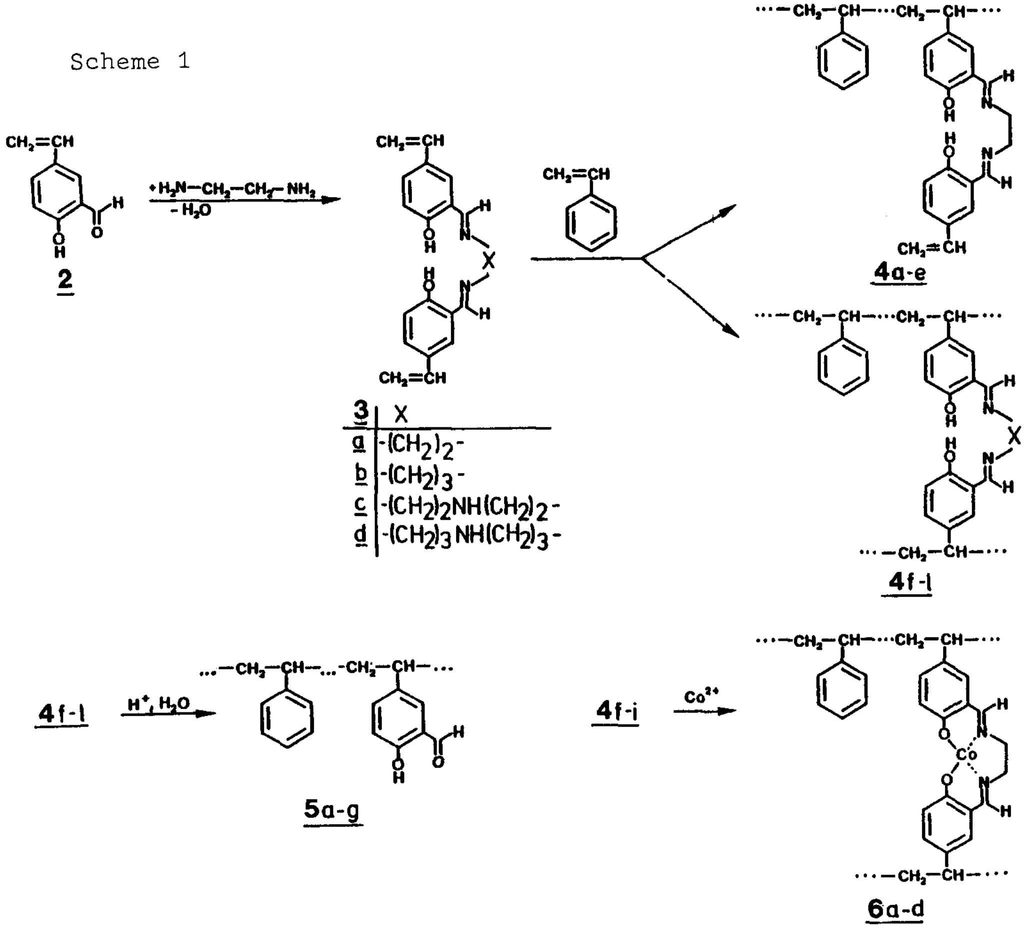
[a] Part 5: Ref. 1).

Scheme 1



That 3a-d are built into the polymers 4a-l can be shown by the IR spectra. Besides the polystyrene absorptions there are strong absorptions at 1625 cm^{-1} ν(C=N) and 1275 - 1280 cm^{-1} ν(C-O). The polymers 4k and 4l exhibit additional absorptions at 3300 cm^{-1} which can be traced to the ν(N-H) absorption of the monomers 3c and 3d.

The IR spectra of the soluble polymers 4a-e exhibit high intensities for the unreacted vinyl group (Ref. 11) at 1000 cm^{-1} (3a at 990 cm^{-1}) and 1630 cm^{-1} (together with (C=N)). Also the unsoluble 4f-l show these absorptions with low intensity due to residual vinyl groups.

In the next step the copolymers 4f-i, which are crosslinked as a result of the bifunctional character of 3a, react with cobalt(II)-acetate·$4H_2O$ to give the metal containing 6a-d. That the reaction is conducted quantitatively can be monitored by e appearance of a new absorption band at 1300 cm^{-1} in the IR trum. The phenolic ν(C-O) absorption at 1275 cm^{-1} disap-
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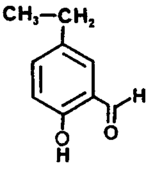
The synthesis beginning with 3 and leading to the metal-containing polymer bound chelates 6 described in Scheme 1 is faster and more elegant than the method described in Ref. 1, since the complicated polymer analogous reaction steps can be avoided.

Direct copolymerization of Co-chelates of divinylsalen 3a is also interesting. Even the case of Co(II) introduction into 3a (DMF at 353 K) resulted in the polymerization of vinyl groups leading to dark colored unsoluble products. Therefore this way of obtaining polymer bound chelatesis not practicable.

COPOLYMERISATION BEHAVIOUR

To determine the copolymerization parameters model substances 7 and 8 were used. The built in ratios were obtained with the aid of UV-spectroscopic extinction coefficients taking the law of Lambert-Beer into consideration. The extinction coefficients in the concentration range of $2\text{-}5\cdot 10^{-4}$ mol/l in DMF are as follows for λ/nm (ε) $l\cdot mol^{-1}$. 7: 332 ($3.8\cdot 10^3$); 8: 322 ($8.2\cdot 10^3$). The copolymers absorb at λ/nm 322 (4) and 332 (5).



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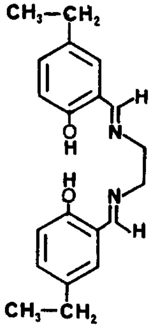

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Taking into account the different inserted monomer concentrations $[M_1]/[M_2]$ and the calculated concentrations $[m_1]/[m_2]$ of the monomers in the copolymers the parameters were determined after graphic evaluation according to the methods of Fineman and Ross (Ref. 11) and Gibb and Barton (Ref. 13) (Table 1). The values $r_1 = 1.6$ and $r_2 = 1.80$ (relative to one double bond for the monomers styrene (M_1) and 3a (M_2) to the soluble copolymers 4a-e (reaction time 2 h) result in a relatively higher reactivity of one double bond in 3a towards styrene (Tab. 1). In case of polymerization to high yield using the pair styrene/3a (reaction time 168 h) crosslinking resulting in the polymers 4f-l occurs. The copolymerization parameters of the copolymers 4f-i were determined after saponification to the soluble copolymers 5a-d. This leads to $r_1 = 0.50$ and $r_2 = 1.24$ (calculated according to Gibb and Barton). Under ass tion of total crosslinking these values show high reacti of double bonds in 3a. Polymerization of 3b-d with sty copolymers 4j-l which after saponification give 5e-g in high reactivity of styrene (Tab. 1).

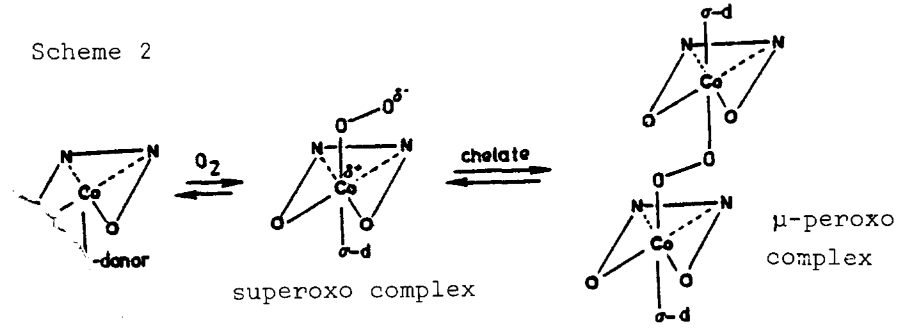
Tab. 1. Composition of copolymers 4, 5 and 6

Copolymer 4, 5 from styrene (M_1) and 3 (M_2)					Copolymer 6 from 4			
No 4	Polymerisation conditions t(h)	$[M_1]/[M_2]$(3a-d)	resulting polymer yield 4 (%)	$[m_1]/[m_2]$ determ. in 4 or 5	No 6	inserted molar ratio Co/4	Co cal(%)	Co fd(%)
a	2	25 (3a)	23	19.0 (4a)				
b	2	40 (3a)	22	28.4 (4b)				
c	2	50 (3a)	22	39.1 (4c)				
d	2	75 (3a)	22	61.9 (4d)				
e	2	100 (3a)	22	77.4 (4e)				
f	168	10 (3a)	53	10.4 (5a)	a	2	4.20	5.72
g	168	25 (3a)	51	25.2 (5b)	b	2	1.98	3.20
h	168	50 (3a)	68	51.0 (5c)	c	2	1.06	1.60
i	168	100 (3a)	66	100.4 (5d)	d	2	0.55	0.84
j	168	25 (3b)	54	12.1 (5e)				
k	168	25 (3c)	82	11.5 (5f)				
l	168	25 (3d)	44	8.3 (5g)				

Dioxygen uptake

In contrast to Fe(II)porphyrins, Co(salen) reversibly forms binuclear μ-peroxo complexes with O_2 at 293 K either in solution (polar, aprotic solvents) or in the solid state (s. lit. notes in Ref. 1). Covalently polymer bound Co-Schiff's base chelates are therefore of great interest as stable, regeneratable dioxygen carries. The O_2 uptake of suspensions of such chelates described in Ref. 1 and this paper was monitored by volumetric measurements in DMF (as solvent and donor ligand) at 293 K. The O_2 binding of low molecular Co(salen) leads to a binuclear complex (molar ratio O_2/Co=0.5) (Tab. 2, Scheme 2). In contrast the high O_2/Co ratios of the covalently polymer bound cobalt chelates makes the reversible formation of mononuclear superoxo complexes (molar ratio O_2/Co=1) likely. Therefore the chelate centers in the polymer were separately distributed onto the polymer carrier, thereby prohibiting binuclear complex formation. The rates of O_2 fixation of the polychelates are comparable with low molecular Cosalen. The reversibility of the O_2-binding of the polychelates is also shown by the fact that the polymers do not have to be stored under inert gas. Heating to 353 K leads to polymers active in O_2-binding.

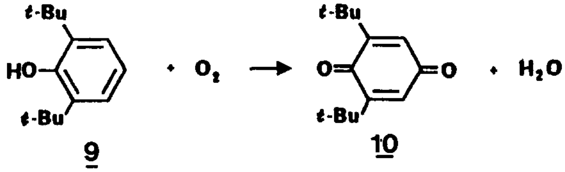
Scheme 2



Oxidation of 2,6-di-tert-butylphenol 9

The oxidation of various phenols using Co(salen) as catalyst leads mainly to the corresponding quinones (s. lit. notes in Ref. 1). One main step of the complicated mechanism is H-radical abstraction from the phenol to the mononuclear O_2-complex of the Schiff' s base chelate.
Tab. 3 compares the catalytic activity of various covalently polymer bound chelates and low molecular Co(salen) in the oxidation of 9 using Co(salen) as catalyst (scheme 3). 97 % of the quinone 10 and 3 % of the corresponding diphenoquinone were obtained. Inserting the polychelates as catalysts only 10 is formed showing low selectivity of the polymers. Generally, the activities of the polychelates are slower in comparison with the low molecular chelate. This fact is not connected to the dimished reactivity of the chelate centers, because extension of the reaction time from 20 h to 72 h increases the yield (Tab. 3). In the case of the polychelates as catalysts the oxidation is diffusion controlled showing a direct linear relation between the volume swelling factor of the polymers and yield of 10 (Ref. 6). Summarizing, the covalently polymer bound chelates combine rapid O_2-binding with good catalytic activity and high reversibility in repeated use (Tab. 2, 3).

Scheme 3



Tab. 2 Oxygen uptake of Co(salen) and covalently polymer bound chelates at 293 K in DMF. Concentration of chelate center: 10^{-3} mol/l.

chelate	oxygen uptake 90% t(min)	O_2/Co	end value t(min)	O_2/Co
Co(salen)	6	0.47	10	0.52
8b in Ref. 1	2	0.77	60	0.86
8c in Ref. 1	1	0.78	45	0.87 a)
8f in Ref. 1	4	0.80	30	0.89
8e in Ref. 1	0.5	0.83	30	0.92 b)
6a	60	0.99	300	1.1
6d	0.5	0.86	5	0.96

a) 2. measurement: 0.87; 3. measurement: 0.92
b) 2. measurement: 0.97; 3. measurement: 0.93

Tab. 3 Oxidation of the phenol 9 with Co(salen or covalently polymer bound chelates as catalysts in DMF at 293 K. Reaction time 20 h. Molar ratio of 9 to chelate centers= 25.

chelate	yield 10 (%)
Co(salen)	97 a)
8b in Ref. 1	17,5
8c in Ref. 1	27
8e in Ref. 1	42
8f in Ref. 1	64
8g in Ref. 1	69 b,c)
6a	9
6b	13
6c	18
6d	26

a) reaction time 2 h; 3 % of corresponding diphenoquinone
b) yield of 10 after 72 h: 95 %
c) repeated use of 8g: 2. time 71 %; 3. time 70 %.

EXPERIMENTAL

Used instruments: IR (Perkin Elmer 577). UV/VIS (Perkin Elmer 544. ^{1}H-NMR (Varian EM 360). MS (MAT CH 7); all low molecular compounds were identified by MS.
Cobalt analyses s. Ref. 1.
All reactions were carried out under dry argon or nitrogen, with dry solvents and reagents free of molecular oxygen. AIBN is recrystallized from ether and dried under reduced pressure. Styrene was destabilized and distilled before use (Ref. 14).

General procedure for the synthesis of divinylsalenes 3a-d (3a: 4,4'divinyl-2,2'-ethylenebis(nitrilo methylidyne)diphenol): To 44 mmol of 2 (Ref. 15) in 25 ml ethanol a solution of 22 mmol of the diamine component in 10 ml ethanol was added under vigorous stirring. The reaction mixture was refluxed for 30 min, cooled and the precipitated yellow colored products 3a,b were filtered off. 3a and 3b were washed several times with ethanol and dried over night at 313 K over KOH pellets. The oily products 3c and 3d crystallized by cooling after evaporation of the solvents.

3a: yield 71 %, Fp. 452 K.
UV (DMF): λ_{max}/nm= 332.
IR (KBr, cm^{-1}): 2920, 2840 (CH$_2$), 1630 (C=N), 1280 (C-O)
^{1}H-NMR (CDCl$_3$): δ= 8.45 (s; CH=N), 7.4 - 6.8 (m; ar), 6.75 - 6.35 and 5.7 - 4.9 (m; vinyl), 3.9 (s; X). Intensity ratio 1:3 :1:2:2.

$C_{20}H_{20}H_2O_2$ (320.4) calc. C 74.92 H 6.39 N 8.79
found C 74.29 H 6.28 N 8.74

3b: yield 67 %, Fp. 383 K.
UV (DMF): λ_{max}/nm= 334. IR s. 3a.
^{1}H-NMR (CDCl$_3$): δ= 8.35 (s; CH=N), 7.4 - 6.8 (m; ar), 6.75 - 6.35 and 5.7 - 4.9 (m; vinyl), 3.5 - 3.75 (m; X). Intensity ratio 1:3:1:2:3.

$C_{21}H_{22}N_2O_2$ (334.4) calc. C 75.43 H 6.63 N 8.38
found C 75.29 H 6.63 N 8.65

3c: yield 53 %, Fp. 340 K.
UV (DMF): λ_{max}/nm= 335.
IR (KBr, cm^{-1}): 3300 (N-H), 2920, 2840 (CH$_2$), 1630 (C=N), 1280 (C-O).
^{1}H-NMR (CDCl$_3$): δ= 8.33 (s; CH=N), 7.4 - 6.4 (m; ar), 6.8 - 6.4 and 5.76 - 5.0 (m; vinyl), 3.8 - 3.6 and 3.1 - 2.9 (m; X). Intensity ratio 1:3:1:2:2:2.

$C_{22}H_{25}N_3O_2$ (363.5) calc. C 72.70 H 6.93 N 11.56
found C 73.03 H 7.04 N 11.60

3d: yield 47 %, Fp. 318 K.
UV, IR s. 3c.
^{1}H-NMR (CDCl$_3$): δ= 8.3 (s; CH=N), 7.4 - 6.3 (m; ar), 6.8 - 6.3 and 5.7 - 4.9 (m; vinyl), 3.75 - 3.50 and 2.7 - 2.4 (m; X). Intensity ratio 1:3:1:2:2:4.

$C_{24}H_{29}N_3O_2$ (393.5) calc. C 73.62 H 7.47 N 10.73
found C 70.70 H 7.56 N 10.93

Copolymers 4: A polymerization tube was charged with the monomers styrene and 3 in various concentrations with 0.5 mol % AIBN and toluene (Tab. 1). After three freeze-thaw cycles the ampoules were sealed and heated at 373 K for 2 h and 168 h. The soluble copolymers 4a-e were precipitated by methanol. The unsoluble copolymers 4f-1 were filtered after being taken up in methanol.

IR (KBr, cm^{-1}): 1625 (s; C=N), 1275 (m; C-O), absorptions of polystyrene.
UV (DMF):λ_{max}/nm (4a-e)= 322.

$[(C_8H_8)_{10,4}C_{20}H_{20}N_2O_2)]_n$ $(1393.5)_n$

calc.	C 88.95	H 7.47	N 2.01
found	C 88.1	H 7.4	N 1.7

Saponification of 4f-1 to 5a-g: The copolymers were treated with 20 % acetic acid in toluene at 353 K. After 72 h the products were precipitated in methanol and treated with methanol in a Soxhlet apparatus for 24 h. The quantitatively obtained yellow products were dried in vacuo at 333 K.

IR (KBr, cm^{-1}): 1650 (s, C=O), 1275 (m, C-O) absorptions of polystyrene.
UV (DMF): λ_{max}/nm = 332.

Cobalt-chelates 6a-d from 4f-1: Approximately 1 g of the copolymers 4 were treated with a double amount of cobalt(II)acetate·$4H_2O$ (Tab. 1) in 50 ml oxygen free DMF for 24 h at 353 K under argon. The dark brown products precipitated. After filtration the products were treated with methanol in a Soxhlet apparatus for 24 h under inert conditions and dried at 353 K.

IR (KBr, cm^{-1}): 1610 (s; C=N); 1525 (m; C=C), 1300 (m; C-O); 1130 (w; C-N), absorptions of polystyrene.

$[(C_8H_8)_{10,4}C_{20}H_{18}CoN_2O_2]_n$ $(1460,4)_n$

calc.	C 84.8	H 6.97	N 1.92
found	C 83.4	H 6.8	N. 2.0

2-Hydroxy-5-ethylphenol (7) (Ref. 16); yield 22.3 %.
UV (DMF): λ_{max}/nm= 332.

4,4'-Diethyl-2,2'-ethylenebis(nitrilomethylidyne)diphenol) (8): The compound was prepared according to the procedure for the synthesis of 3.

UV (DMF): λ_{max}/nm= 322.
IR (KBr, cm^{-1}): 2950, 2920 (CH), 1630 (C=N); 1580 - 1430 (ar) 1280 (C-O).
^{1}H-NMR ($CDCl_3$) δ: 8.3 (s; CH=N), 7.35 - 6.8 (m; ar), 3.9 (CH_2), 2.6 (CH_2); 1.2 (CH_3).

Dioxygen binding: The measurements were carried out with a slightly modified Warburg apparatus (B. Braun, Melsungen, FRG) at 293 K as described in detail in Ref. 6.

Catalytic reactions: The oxidation were followed by measuring the oxygen consumption in a microhydrogenation apparatus according to Marhan (O. Fritz GmbH, Normag-Hofheim, FRG) at 293 K. Additionally the conversion was followed by ^{1}H-NMR. Details are described in Ref. 6.

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