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Polymeric Schiff Base Chelates and Their Precursors
1. Synthesis of Covalently Bound Co(Salen) Through Alkylation of Polystyrene

D. Wöhrle

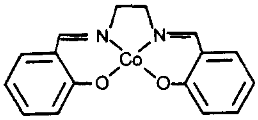
Abteilung für Chemie, Universität Bremen, Bibliothekstraße, NW 2, 2800 Bremen, Federal Republic of Germany

SUMMARY

Covalently polymer bound Co(salen) 6a-c was synthesized starting from two macroporous resins 2a,b and a linear polystyrene 2c. Reaction of 2a-c with 5-chloromethylsalicylaldehyde to 3a-c, then with 1,2-diaminoethane to 4a-c and then with salicylaldehyde led to the metal free ligands 5a-c which could be metallized to 6a-c.

INTRODUCTION

Co(salen) 1 shows excellent properties for binding of small molecules (reversible: O_2; irreversible: NO (ref. 1-3). Furthermore, 1 is active as catalyst (oxidation of organic compounds like indoles, xylenoles) (ref. 4). Until now there is no report about 1 covalently bound to a polymer chain which will be profitable for the mentioned reactions. When 1 was coordinated to a polymer-ligand (copolymer of styrene and vinylpyridine), it formes a stable oxygenated complex at room temperature more readily than the low molecular weight complex 1 (ref. 5,6). Actually, we describe a simple synthesis of a covalently bound of 1 to polystyrene. The activity of these polymers will be considered in a succeeding paper.



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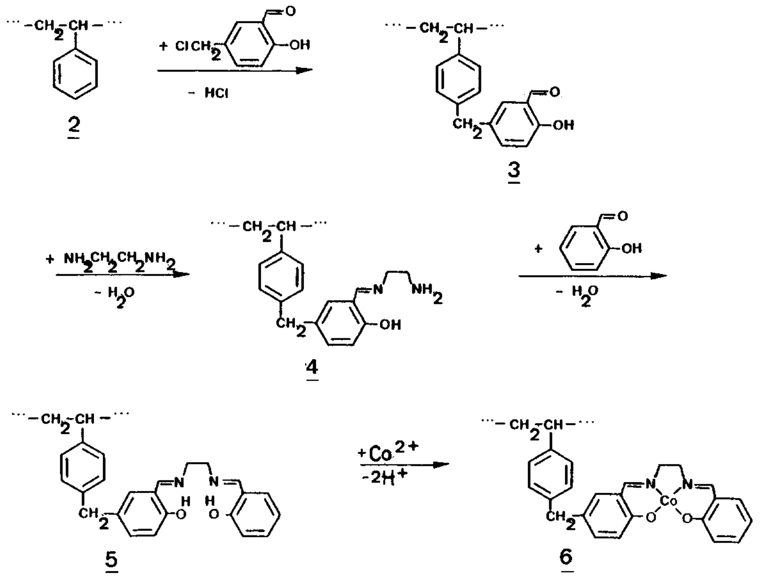
RESULTS AND DISCUSSION

As starting materials two macroporous unsoluble resins 2a,b and a linear polystyrene 2c are used. Friedel-Crafts-alkylation of 2a-c with 5-chloromethylsalicylaldehyde in the presence of an excess of $AlCl_3$ in nitrobenzene lead to the alkylated light yellow polymers 3a-c. Corresponding to the high yield of such a alkylation (ref. 7) the amount of chloromethylsalicylaldehyde was chosen in order to give 10 % alkylation. Starting from 2c a voluminous swollen polymer 3c was obtained in nitrobenzene. Typical IR-absorptions (Fig. 1) for 3a-c - besides polystyrene bands - appear at 1655 (ν(C=O)) and 1280 cm^{-1} (ν(C-O)) indicating covalently bound salicylaldehyde.



After the reaction of 3a-c with 1,2-diaminoethane to the polymers 4a-c only the absorption at 1655 cm^{-1} disappears and a new band at 1630 cm^{-1} (ν(C=N)) is observed. In addition, a band with low intensity at 1225 cm^{-1} (ν(C-N)) appears, which disappears during the reaction of 4a-c with salicylaldehyde to give the polymers 5a-c containing the salen-ligand.

The introduction of Co^{2+} in 5a-c leads to the metallized polychelates 6a-c. In contrast to the metallization in ethanol the reaction in DMF is complete. Starting from the alkylated polymers 3a-c the reaction sequence to 6a-c is complete and nearly every tenth till fifteenth benzene ring contains a covalent bond to a Co(salen). In the IR-spectrum of 6a-c some new typical strong absorptions of the Co(salen)-complex are observed: 1560-1590 cm^{-1}, 1430-1400 cm^{-1}, 1330 cm^{-1}.

Consequently, the described reactions are a simple method to prepare covalently bound Co(salen). Therefore this method must be of great interest for the fixation of the great number of other known N_2O_2-chelates, too.

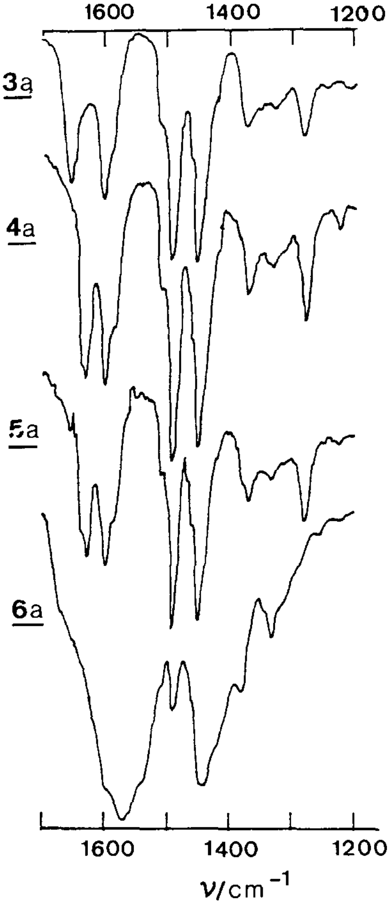


Fig. 1 IR-spectra (in KBr) of 3-6

EXPERIMENTAL

All reactions are carried out under dry argon.
Macroporous resin 2a: 63 g styrene, 54 g divinylbenzene (as a mixture with 50 % ethylvinylbenzene), 0.8 g dibenzoylperoxide, 150 g hexane, 60 g toluene, 1200 ml H_2O, 3 g betonite, 3 g gelatin, 3 g NaCl; polymerisation at 80°C for 16 h (ref. 8).

Macroporous resin 2b: 83 g styrene, 30 g divinylbenzene (as a mixture with 50 % ethylvinylbenzene), 0.8 g dibenzoylperoxide, 120 g hexane, 16 g toluene; 1200 ml H_2O, 3 g betonite, 3 g gelatin, 3 g NaCl; polymerisation at 80°C for 16 h (ref. 8).

2c: (η_{inh}= 0.37-0.38 dl/g at 30°C in benzene).

3a-c: 2.1 g (12 mmol) 5-chloromethylsalicylaldehyde was dissolved in 40 ml of dry chloroform and 10 g 2a,b were added. After the suspension was shaken weakly for 1h, the solvent was evaporated at 30°C under vacuum. Under slow stirring a solution of 2 g (15 mmol) $AlCl_3$ in 40 ml dry nitrobenzene was added. For the reaction of 2c the polymer was dissolved in 150 ml nitrobenzene and then adding 2.1 g of the aldehyde and afterwords 3 g $AlCl_3$ in 40 ml nitrobenzene dropwise. After three days reaction time at 70°C the reaction mixtures were poured into methanol. Intensive washing with methanol/conc. HCl (1:1) and treatment with methanol in a soxhlet-apparatus led to the pure 3a-c. Yields after drying at 70°C: 10.7-10.9 g.

3a calculated: $(C_8H_8)_5\cdot(C_{10}H_{10})_2\cdot C_8H_7\cdot C_8H_7O_2$

C 89.6 H 7.3

3a found: C 88.7 H 7.6

3c calculated: $(C_8H_8)_{13}\cdot C_8H_7\cdot C_8H_7O_2$

C 90.6 H 7.4

3c found: C 89.0 H 7.5

4a,b: 7.5 g of 3a,b were suspended in 70 ml benzene and heated after addition of 4.5 g (76 mmol) 1,2-diaminoethane 24 h under reflux. Purification was achieved by treatment with benzene in a soxhlet-apparatus. Yields of 4a,b after drying at 70°C: 7.5 - 7.6 g.

4a calculated: $(C_8H_5)_5\cdot(C_{10}H_{10})_2\cdot C_{10}H_{13}N_2O$

C 88.3 H 7.6 N 2.6

4a found: C 87.6 H 7.7 N 2.1

4c: A voluminous swollen solution of 7.5 g 3c in 150 ml benzene was refluxed for 24 h in the presence of 4.5 g (75 mmol) diaminoethane. The solution was poured in methanol and after filtration the polymer 4c was treated with methanol in a soxhlet-apparatus. Yield 7.5 g.

4c calculated: $(C_8H_8)_{13}\cdot C_8H_7\cdot C_{10}H_{13}N_2O$

C 89.7 H 7.6 N 1.7

4c found: C 88.9 H 7.6 N 1.9

5a-c: 5 g of 4a-c in 70 ml benzene were heated in the presence of 3.1 g (25 mmol) salicylaldehyde for 24 h. After purification with benzene in a soxhlet apparatus and drying at 70°C the yields of 5a-c are 5.2 - 5.3 g.

5a calculated: $(C_8H_8)_5\cdot(C_{10}H_{10})_2\cdot C_8H_7\cdot C_{17}H_{17}N_2O_2$

	C 87.6	H 7.2	N 2.4
5a found:	C 87.3	H 7.6	N 2.0

5c calculated: $(C_8H_8)_{13}\cdot C_8H_7\cdot C_{17}H_{17}N_2O_2$

	C 89.2	H 7.4	N 1.6
5c found:	C 89.2	H 7.6	N 1.8

Metallization of 5a-c to 6a-c in ethanol and DMF: 2.5 g of 5a-c were heated in 150 ml ethanol or DMF in the presence of 0.7 g (3 mmol) cobalt-II-acetat·4 H_2O for 24 h at 80°C. Using ethanol as solvent 1.5 g sodium acetat was added. The reaction products were treated with ethanol in a soxhlet apparatus for 24 h under argon, dried at 70°C and stored under argon. Yields 2.5 - 2.6 g.

6a calculated: $(C_8H_8)_5\cdot(C_{10}H_{10})_2\cdot C_8H_7\cdot C_{17}H_{15}CoN_2O_2$

	C 83.5	H 6.7	Co 4.8	N 2.3
6a (DMF) found:	C 83.5	H 6.6	Co 3.9	N 1.7
6a (ethanol) found:	C 85.1	H 7.0	Co 3.4	N 1.4
6b (DMF) found:			Co 4.5	
6b (ethanol) found:			Co 2.3	

6c calculated: $(C_8H_8)_{13}\cdot C_8H_7\cdot C_{17}H_{15}CoN_2O_2$

	C 86.6	H 7.0	Co 3.2	N 1.6
6c (DMF) found:	C 85.3	H 6.9	Co 3.1	N 1.4
6c (ethanol) found:	C 86.7	H 7.3	Co 1.4	N 1.3

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