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Analysis

Circular Dichroism Study

Palladium (II) Complexes with Polymer Bound S-Methyl-L-Cysteine

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Summary

N methacryloyl-S-methyl-L-cysteine (SMC) homopolymer along with a copolymer with methacrylic acid were prepared in the purpose of studying their complexation with Pd(II). The circular dichroism study showed that the binding of SMC residue to a polymeric chain does not change the coordination donor set of Pd complexation, i.e. |N,S| . The number of side chains per metal ion involved in the complexation depends on the molar fraction of SMC in the case of the copolymer and on the SMC/Pd ratio for both homopolymer anc copolymer. The variation of viscosity when adding Pd(II) suggests the formation of intramolecular loops.

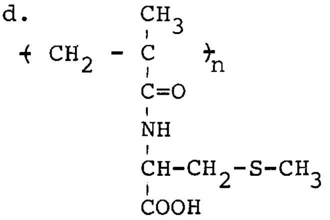
Introduction

The studies on the S-alkyl-cysteine complexes of Pd(II) and Pt(II) revealed several interesting structural and spectroscopic properties, among others resulting from the formation of a chirality center on thioether sulfur atom (KOZLOWSKI et al. (1980); DECOCK et al. (1982); KUBIAK et al. (1980); HADJILIADIS et al. (1982)).The {N,S} coordination mode is characteristic for this kind of complexes even in strongly acidic solutions.

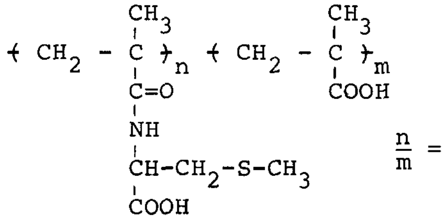
The increasing interest in the immobilized coordination complexes (TSUCHIDA and NISHIDE, 1977) has inspired us to study the coordination ability of polymer bound S-Methyl-cysteine. Though aminoacids are well known as the ligands, there are only few works on the complexation of polymers with aminoacids residues bound to their polymer side chain (SNYDER (1972) ; DAVANKOV (1974); KORDE (1981); IMANISHI and KINIWA (1981); TSUCHIDA (1976)).

In this communication, we present the CD study of Pd(II) coordination with homopolymer, N-methacryloyl-S-methyl-L-cysteine (I) and its copolymer analogue (II) with methacrylic acid.

I



$$-\!\left(CH_2-\overset{CH_3}{\underset{\substack{|\\C=O\\|\\NH\\|\\CH-CH_2-S-CH_3\\|\\COOH}}{\overset{|}{C}}}\right)_{n}$$



$$-\!\left(CH_2-\overset{CH_3}{\underset{\substack{|\\C=O\\|\\NH\\|\\CH-CH_2-S-CH_3\\|\\COOH}}{\overset{|}{C}}}\right)_{n}-\!\left(CH_2-\overset{CH_3}{\underset{\substack{|\\COOH}}{\overset{|}{C}}}\right)_{m}$$

II

$\frac{n}{m} = \frac{1}{2}$

Experimental

N-methacryloyl-S-methyl-L-cysteine was prepared according to (KULKAMI and MORAWETZ (1961)). 1/20 mole of S Me cyst (6,75 g) was converted into the sodium salt by addition of 1/20 mole (2 g) of sodium hydroxyde and 10 ml of water, then cooled on ice. 1/20 mole (7,7 g) of methacryloyl chloride and 10 ml of 5 N sodium hydroxyde were added dropwise simultaneously under vigourous stirring. After one hour at room temperature, the mixture was acidified to pH 1.5 - 2 with 6 N hydrogen chloride. N methacryloyl-S methyl-L-cysteine was extracted with ethyl acetate. The solution was dried over magnesium sulfate, filtered off and the product was recovered by evaporation of the solvent under reduced pressure - yield 50 % - In infrared, the amide I band is located at 1650 cm^{-1}.

Poly(N-methacryloyl-S-methyl-L-cysteine)

The polymerization was carried out during 18 h under vacuum at 65°C, using a solution of monomer in dimethylformamide and 2,2'azoisobutyronitrile (AIBN) (1 % in mole). Prior to polymerization, the mixture was deaerated by three cycles of freezing, pumping and thawing. The homopolymer was dialyzed against ethyl alcohol and then water. It was recovered by freeze drying.

Poly(N methacryloyl S-methyl-L-cysteine-co-methacrylic acid

The procedure was similar to that used for homopolymer from N methacryloyl-S-methyl-L-cysteine (0.5 10^{-2}mole, 1 g) and methacrylic acid (0.5 10^{-2} mole, 0.43 g) with AIBN as initiator during 5 H.

The copolymer was dialyzed against water, ethyl alcohol and against water, recovered by freeze drying. The composition of the copolymer was determined by element analysis.

N : 3.26 %, S : 8.80 % id est 68 % of methacrylic acid and 32 % of N methacryloyl-S-methyl-L-cysteine (molecular ratio).

K_2PdCl_4 was obtained by crystallization of KCl and $PdCl_2$ solutions containing HCl.

CD spectra were recovered on a Mark III Jobin Yvon dichrograph in the 450-200 nm region with polymer concentration 5 10^{-3}mole/litre.

Results and discussion

CD spectrum of an aqueous solution of homopolymer PNM SMC at pH ∿7 (Pd : SMC molar ratio 1:4) consists of four bands at 340, 285, 267 and 207 nm and a shoulder at ∿ 225 nm (Table 1)

TABLE 1

CD spectra of Pd (II) complexes with homopolymer bound S-methyl cysteine.

	pH	λ (mn)	Δε
	7	207	- 5.5
Homopolymer/Pd		225 (sh)	- 2.1
1 Pd/4S		267 (b)	+ 1.06
		285 (b)	+ 1.13
		340	- 1.10
	10	199	- 1.36
		204	- 1.36
		225	+ 0.54
		241	+ 0.72
		274	+ 0.30
		290	+ 0.40
		337	- 0.66

The 340 nm Cotton effect corresponds to the d-d transitions of Pd (A+E transitions (DECOCK et al. (1982))). This energy value strongly suggests the involvement of two nitrogen donors, i.e. two SMC residues, in the metal ion binding (DECOCK et al. (1982); JEZOWSKA-TRZEBIATOWSKA et al. (1978)). The other two bands at 285 and 267 nm are induced due to the metal-sulfur bond formation (DECOCK et al. (1982); KOWALIK et al. (1982); KOZLOWSKI et al. (1983)). The former signal may be assigned as the $\pi S \rightarrow Pd(II)$ charge transfer transition. The other one is considerably broadened and it contains most likely two overlapped transitions i.e. intrasulfur and $\sigma S \rightarrow Pd(II)$ charge transfer transitions (DECOCK et al. (1982)). The increase of pH changes the CD spectra of Pd(II) PNM SMC solutions quite distinctly. The 267 nm band splits into two signals, at pH 10, centered at 274 and 241 nm (table 1). The considerable decrease of Δε values to about half of those found at pH 7 (Table 1) may derive most likely from the variation of the diastereomer distribution. The small variations of the polymer chain conformation between pH 7 and 10 may induce steric changes of the absolute configuration on sulfur donor observed also in model systems (DECOCK et al. (1982); KOZLOWSKI et al. (1983)) The energy pattern of the d-d transition at pH $\sim$ 10 again corresponds to the binding of two aminoacid residues to each metal ion. The {2N, 2S} coordination seems to be predominant in the studied solutions. The cis arrangement of the donor pairs is forced by ligand composition (see formule I) when metal ion binds two adjacent SMC residues.

In all solutions with higher than 1:4 Pd:SMC molar ratio, the precipitation occured at whole pH range. It may suggest that coordination leads to intermolecular aggregate or intermolecular loops responsible for precipitation of the solution. The difference of viscosity between the free and the coordinated homopolymer supports this interpretation (table 3).

The palladium (II) copolymer solutions behave differently than those with Pd PNM SMC. They are clear for the 1:1 molar ratio. The formation of palladium complex is observed at low

TABLE 2

CD spectra of Pd(II) complexes with copolymer bound S methyl cysteine

	pH	λ nm	Δε
Copolymer/Pd			
1Pd/2S	7	205	- 1.96
		211 (sh)	- 1.24
		216 (sh)	- 9.9
		260-280	+ 0.36
		340	- 0.31
		395	+ 0.05
1Pd/1S	2.4	203	- 1.25
		214	- 0.85
		246 (sh)	+ 0.37
		247 (sh)	+ 0.43
		267	+ 0.47
		365	- 0.12
	7.3	205	- 0.15
		220	- 0.2
		247	+ 0.5
		260	+ 0.38
		355	- 0.16
	10.7	205	- 0.5
		212	+ 0.6
		242	+ 0.55
		271	- 0.05
		282	- 0.06
		345	- 0.07

TABLE 3

Viscosity of Homopolymer and Copolymer. conc. 4.10^{-3}g/ml t=25°C

	pH	η_{sp}
Homopolymer	11	0.957
	7.6	0.957
Homopolymer : Pd		
1Pd/4S	9.5	0.283
Copolymer	10	0.489
Copolymer : Pd		
1Pd/2S	8	0.246
	11	0.246
1Pd/1S	8	0.174
	11	0.174

pH range. At pH 2.4, the d-d region exhibits broad band at 365 nm (E) with shoulder at ∿ 385nm (A) (Table 2). The energy values of both d-d transition (A and E) are close to those found for the simple Pd SMC complex (DECOCK et al. (1982)), though the cotton effects are of different signs. Thus it may be concluded that, in these conditions metal ion binds one SMC residue of copolymer ligand via {N, S} donors. The metal sulfur bound formation is also seen in the UV region of CD spectrum, since S → Pd(II) charge transfer transitions are observed at 246 (σS → Pd) and ∿ 270 (πS → Pd) nm. The different signs of Cotton effects of this Pd copolymer complex when compared to Pd SMC derive most likely from the different diastereomer populations in both systems (KOZLOWSKI et al. (1983)) i.e. the polymer chain may distinctly influence the stereochemistry of the metal sulfur bond.

The increase of pH shifts the d-d transitions towards higher energy. The energy variation as well as the major changes in the UV region may derive e.g. from the dimerization of metal ions by OH^- groups (LIM and MARTIN (1976)). The later process is possible for these metal ions in which SMC residue donors occupy only two of four coordination sites.

The formation of 1:2 Pd:SMC subunits is certainly possible in 1:2 molar ratio solutions. The d-d transition at 340 nm may strongly suggest {2N,2S} coordination (DECOCK et al. (1982); KOWALIK et al. (1982); KOZLOWSKI et al. (1983)). The weak cotton effect at 395 nm (table 2) could be assigned as B transition ($B_1 \rightarrow B_2$) which is usually forbidden for D4h symmetry (MARTIN (1974)). The minor concentration of 1:1 Pd:SMC species (395 nm is then A transition of 1:1 complex) in the studied solution can not be excluded though very symmetric 340 nm band does not support such suggestion.

The constant viscosity in Pd - Cp SMC solutions between pH 8 and 11 does not suggest any major overall conformation change of copolymer chain and most of the structural changes around metal ion when e.g. pH is changed seems to be local The metal ion, however, when added to polymer solution causes drastic diminution of viscosity due to its coordination (table 3). It means that complexation leads to a more compact conformation of the macromolecular chain. In the case of 1 Pd/1 S, the CD studies have shown that the main coordination mode is |N, S| but only a few loops originating in |2N, 2S| coordination, which can not be seen by CD, induce a drastic variation of viscosity.

The presented results have shown that binding of SMC residue to polymer chain does not change coordination donor set used in metal ion complexation. Polymer, however, has important influence on the conformation and absolute configuration in the complex unit formed during complexation. The vicinity of two aminoacid residues branched in homopolymer ligand makes very easy formation of 1:2 Pd:SMC complex units due to entropic factor.

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