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Rotational Isomerism in Pd(II) Complexes with S-Methyl-L-Cysteine and Its Derivatives

H. KOZŁOWSKI, Z. SIATECKI, B. JEŻOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław, ul. Joliot-Curie 14, 50-383 Wrocław, Poland

and A. ALLAIN

Institute of Chemistry, L. Pasteur University, 4 B. Pascal st., 67-000 Strasbourg, France

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Introduction

Studies of the interactions of Pd(II) and Pt(II) metal ions with some sulfur-containing amino acids have revealed the equilibrium of a few chemical species in solutions, at any pH range [1–4].

Both X-ray and NMR results indicated that the S-methyl-L-cysteine sulfoxide (SOMC) and the S-methyl-L-cysteine methyl ester (SMCOMe) are coordinated to metal ions through the S and N donors. The 1:1 ligand:metal complexes were found to correspond to two isomers, differing by the methyl group arrangement on the asymmetric sulfur center [3, 4]. According to IR, ^{13}C NMR and X-ray crystallographic investigations, the same mode of coordination was concluded for the S-methyl-L-cysteine (SMC) to Pt(II) and Pd(II) ions [2, 5]. These results were found to be in disagreement with those obtained from the rotational conformation analysis with the ^{1}H NMR method in aqueous solutions. According to the proton assignment and the rotamer notation used in our earlier considerations [1], SMC was supposed to bind metal ions through sulfur and nitrogen or carboxyl group. To explain this disagreement, we have decided to reinvestigate the Pd(II)–SMC system in more detail with use of the ^{1}H NMR spectra analysis.

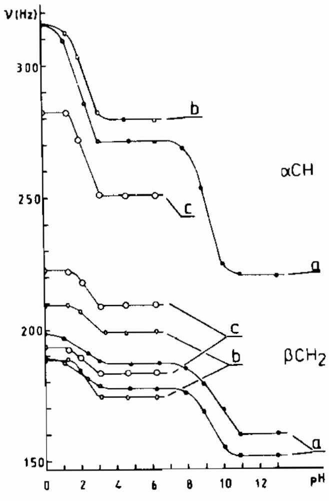

Fig. 1. pH dependence of the chemical shift of A, B, C protons in (a) SMC metal-free ligand, (b) major and (c) minor 1:1 SMC–Pd(II) complexes.

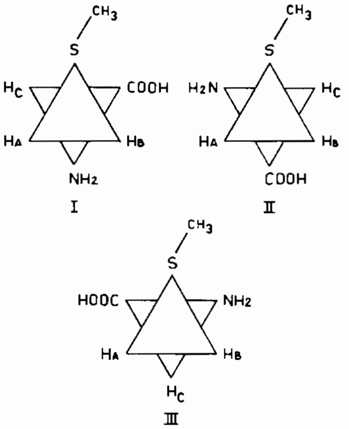

Fig. 2. Rotamer notation.

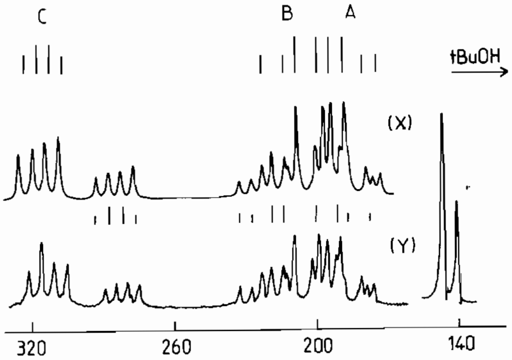

Fig. 3. Experimental (y) and simulated ABC spectra of 1:1 SMC–Pd(II) solutions.

Experimental

1H NMR spectra were recorded on a JEOL 100 MHz JMN-PS-100 spectrometer with tert-butyl alcohol used as internal standard. All NMR spectra were recorded at 25 ± 2 °C. Analysis and simulation of the ABC spectra were carried out on a JEC-6 computer.

^{1}H NMR Spectra of SMC–Pd(II) Solutions

The pH dependence of the chemical shifts of the A, B and C protons for metal-free SMC and coordi-

TABLE I. ^{1}H NMR Parameters and Rotamer Populations for S-methyl-L-cysteine and Its 1:1 Complexes with Pd(II) after A and B Proton Chemical Shift Assignment Correction. Chemical shifts are downfield from tert-butanol and they are given in Hz. (1) and (2) label major and minor species found in 1:1 Pd(II)SMC solution, respectively.

Compound	pH		ν_A	ν_B	ν_C	ν_{CH_3}	$\lvert J_{AB}\rvert$	J_{AC}	J_{BC}	p_I	p_{II}	p_{III}
SMC	3–8		177	187	272	92	15.0	8.5	3.5	0.09	0.54	0.37
SMC–Pd(II)												
1:1	3–8	(1)	200	175	281	144	13.3	9.3	4.9	0.21	0.61	0.18
		(2)	184	208	250	137	13.0	9.2	4.6	0.18	0.60	0.22

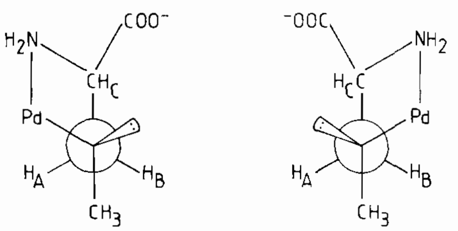

Fig. 4. The two 1:1 isomers looking down the S, C_β bond.

nated SMC in both 1:1 SMC–Pd(II) species is shown in Fig. 1. The α-CH chemical shift variation with pH presents similar titration curves for the carboxylate deprotonation in both Pd(II) species (curves b and c). At pH up to 1.5, the α-CH proton resonance of the minor 1:1 SMC–Pd(II) species (c) is strongly upfield shifted compared to that of the metal-free SMC molecule. Thus SMC ligand besides the sulfur donor is bound to Pd(II) ion through the nitrogen [1, 2]. The α-CH proton resonance of the major 1:1 SMC: Pd(II) species in the pH range 3–7 is downfield shifted compared to that of the free SMC molecule. This latter result and the lack of the influence of Pd(II) ion coordination on the carboxylate deprotonation process (Fig. 1) strongly suggest the binding of the nitrogen donor. Thus, in both species in SMC–Pd(II) solutions, SMC is S,N-coordinated to Pd(II) ion.

The simulation of the ^{1}H NMR ABC spectra of the 1:1 SMC–Pd(II) solution, using the βCH_2 proton assignment made in Fig. 2, produced exactly the experimental spectra (Fig. 3). However, in the major ABC spectrum, the βCH_2 proton assignments have to be inversed (rotamer I ↔ rotamer II) to agree with the S,N-coordination of the ligand to metal ion (Table I). The A proton environment in the first 1:1 species is the same as that for the B proton in the second species considering the SCH_3 group and lone electron pair positions on the sulfur atom (Fig. 4). The latter situation explains the existence of two rather different ABC spectra as far as the A and B proton chemical shifts are considered [6–9]. Thus, the two species of 1:1 SMC–Pd(II) solutions are found to be the two S,N-coordinated diastereoisomers containing the different chiral center on the sulfur atom. These results were confirmed by the studies in solution and in the solid state made for Pd(II) complexes with S-methyl-L-cysteine sulfoxide [3] and S-methyl-L-cysteine methyl ester [4]. The three species found in solutions for 1:2 metal–ligand systems correspond to the different isomers obtained by inversion of the sulfur atom, in which the SMC molecule is also S,N-coordinated to metal ion. Pt(II)–SMC compounds have a similar structure as Pd(II)–SMC ones as was stated by Erickson *et al.* [10]. Thus the exchange process described earlier [1] is due to the inversion process on the sulfur atom which involves the lone electron pair mechanism on the asymmetric sulfur center [4, 6–9].

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