CD Spectra of Palladium(II) Methionine Complexes

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Received May 20, 1982

The formation of the metal–thioether sulfur bond enriches considerably the UV region of the CD spectra [1, 2], which results in the creation of the new chirality center on sulfur. The important feature of these spectra seems to be the possible intrasulfur transition [1] which may be activated by the new assymetric center on sulfur atoms [1–5].

In Pd(II) complexes with S-methyl L-cysteine studied earlier [1], the C_α center may also contribute considerably to the Cotton effect of the intrasulfur transition [6]. To diminish the latter possibility we have studied a series of Pd(II) complexes with methionine residues in which the perturbation of sulfur atoms by the C_α optical center is too small to be seen in CD spectra.

Experimental

Methionine and its peptides were obtained from Fluka. K_2PdCl_4 was used as a metal ion source.

The absorption spectra were recorded on a Beckman UV 5240 spectrophotometer. The CD spectra were measured on an automatic recording spectropolarimeter JASCO-20.

Solutions with a molar ratio of Pd(II)/ligand 1:1 were used for all measurements with the metal ion concentration equal to 5×10^{-3} *M*.

Results and Discussion

The CD spectra of L-methionine residue of the metal-free ligands (Table I) resemble those of aliphatic hydrocarbon amino-acid residues (see *e.g.* [6]). They may differ, however, from the CD spectra observed for S-methyl L-cysteine residue [1, 6]. In the latter case, the intrasulfur transitions become active as was observed for several peptides [1, 6].

Earlier studies have shown that the methionine residue binds to Pd(II) via {NS} donor set acting as

TABLE I. CD Spectra of Methionine Containing Ligands and their Palladium(II) Complexes.

Compound	pH	λ, nm	Δε
Met	6.2	200	+1.68
Gly–Met	6.8	216	+0.26
		200	–
Met–Gly	7.1	200	+3.53
Met–Val	6.3	215 sh	–1.43
		210	–1.69
Met–Thr	7.7	209	–1.93
Pd Met	5.8	407	+0.2
		267	–1.61
		260	–1.52
		230 sh	+1.02
		209	+2.28
Pd Gly–Met	7.2	415	–0.11
		334	–0.33
		300	+0.14
		267	–1.04
		247	+0.61
		232	–0.17
		212	+2.42
Pd Met–Gly	7.0	408	+0.39
		319	+1.22
		258	+2.58
		228	–6.02
Pd Met–Val	7.8	406	+0.03
		346	–0.27
		253	+5.28
		214	–17.75
Pd Met–Thr	7.0	415	+0.08
		323	–0.44
		278	–0.61
		253	+4.23
		214	–18.50

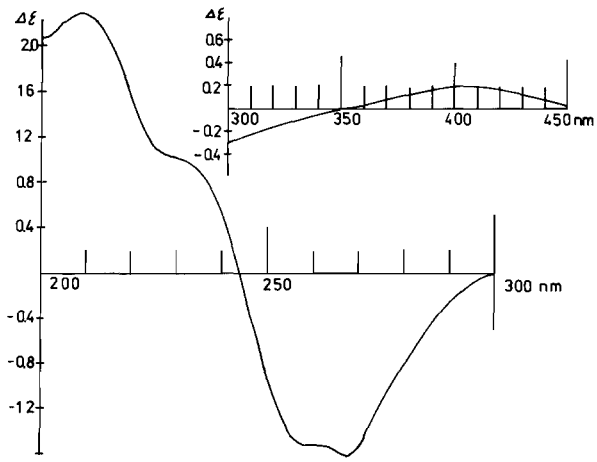

Fig. 1. CD spectrum of PdMet complex at pH 5.8.

0020-1693/82/0000-0000/$02.75

a bifunctional ligand [7, 8], and the same coordination mode is involved for the systems studied in this work.

The CD spectrum of Pd(II) methionine complex exhibits one broad positive d–d band at 407 nm which consists of overlapped A and E transitions [1] (Table I, Fig. 1). The UV region consists of the four Cotton effects at 267, 260, 230 and 209 nm. The latter band also observed for metal-free methionine could be assigned as the intraligand transition within carbonyl chromophore. The other three bands are characteristic for the complex molecule and their energies resemble those of the PdSMC complex [1]. The 230 and 267 nm transitions are $S_\sigma \rightarrow$ Pd and $S_\pi \rightarrow$ Pd charge transfer transitions respectively [1, 9, 10]. The 260 nm Cotton effect derives most likely from the intrasulfur transition activated by the metal ion binding to sulfur donor which becomes the new ligand assymetric center.

Also in Pd Gly–Met complex with {NNS} coordination mode [8], the formation of metal sulfur bond leads to the creation of three characteristic bands for complex molecule in the UV region (Table I). Two charge transfer transitions are centered at 265 ($S_\pi \rightarrow$ Pd) and 231 nm ($S_\sigma \rightarrow$ Pd) and the intrasulfur band at 246 nm. The d–d region of Pd Gly–Met complex consists of three extrema at 415, 334 and 300 nm. The latter two bands derive most likely from the splitting of the E transitions.

The CD spectra of Pd(II) complexes with dipeptides containing methionine as a N-terminal residue (Met–Gly, Met–Val, Met–Thr) differ from those obtained for the Pd Gly–Met (Table I) The main cause of those differences seems to be the differences in the coordination model. Gly–Met binds metal ion via {NNS} donor set forming monomeric complex with two chelate rings, while the other dipeptides with N-terminal Met using the same donor set would rather form the dinuclear complexes with Pd(II) preserving the planar structure around the metal ion [8].

The main differences in the CD spectra (*e.g.* $\Delta\epsilon$ values) of methionine and S-methyl L-cysteine complexes derive from the different chelate ring size and conformations formed by both residues. The presence of the intense intrasulfur transition in the CD spectrum of Pd Gly–Met complex suggests the distinct predominance of one of the diastereoisomers, which was not the case in Pd Gly–SMC [1].

The above results seem to support our earlier conclusion [1] that the metal ion coordination to thioether sulfur activates the new band in the CD spectra derived from the intrasulfur transition. On the other hand, the creation of the chirality center on sulfur would have a major impact on the Cotton effects of the d–d region band (see *e.g.* [4, 5])

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