Chemistry

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EXAFS Study of Pd^{II} Complexes bearing Glycosylated Pyridyltriazole Ligands for Inorganic Pharmaceuticals

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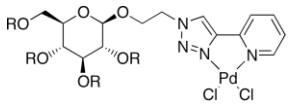
Introduction

Inorganic medicinal chemistry is a rapidly growing field especially for anti-tumor, anti-rheumatism and anti-diabetes treatments. Although metal ions are key element for therapeutic action, a carrier (ligand) is needed to deliver safely into desired parts. In this point of view, we have synthesized ligands bearing sugar moieties which plays an important role in biological events such as cellular recognitions. In this study, we have synthesized novel Pd^{II} complexes (Chart 1) bearing glycosylated pyridyltriazole ligands $\mathbf{L}_1$ and $\mathbf{L}_2$. These structures were established by extended X-ray absorption spectroscopy (EXAFS) measurement using theoretical standards.

Chart 1



$PdCl_2\mathbf{L}_1$ (R = Ac), $PdCl_2\mathbf{L}_2$ (R = H)

Experimentals

The ligands $\mathbf{L}_1$ and $\mathbf{L}_2$ were synthesized as reported previously [1]. The Pd^{II} complexes were prepared by the reactions of $[PdCl_2(CH_3CN)_2]$ with $\mathbf{L}_1$ and $\mathbf{L}_2$ in the mixture of MeOH and H_2O. The Pd-K edge EXAFS measurements were carried out at room temperature in transmittance mode at PF-AR NW-10A. Back-scattering amplitude $F_i(k)$ and phase shift $\Phi_i(k)$ functions (i = Pd–N and Pd–Cl) were calculated by FEFF 8.2 program [2]. All calculations were performed with IFEFFIT program suite [3].

Results and Discussion

Figure 1 shows the Fourier transforms of the EXAFS oscillation at Pd-K edge of $PdCl_2\mathbf{L}_1$ in solid state. Two peaks were found at ca. 1.5 and 1.9 Å (before phase-shift correction). The back-transforms in the range from 1.2 to 2.3 Å was fitted with the standard EXAFS equation taking into account the two single scattering paths between Pd and N, and Pd and Cl, in which the theoretically-derived $F_i(k)$ and $\Phi_i(k)$ functions (i = Pd–N or Pd–Cl) were applied. Table 1 and 2 list the structural parameters. For both cases, the intrinsic loss factors S_0^2 were found to be ca. 1, and the R values were small enough. The interatomic distances r_i were determined to be 2.02(13) and 2.298(3) Å for Pd–N and Pd–Cl, respectively. The r_{Pd-N} and r_{Pd-Cl} values observed in DMF solution were almost same to those of solid state. In addition, the Debye-Waller factors σ_i also keep constant. $PdCl_2\mathbf{L}_2$ showed almost identical EXAFS spectra to that of $PdCl_2\mathbf{L}_1$, and the structural parameters were good in accordance with those derived by X-ray crystallography. Hence $PdCl_2\mathbf{L}_1$ and $PdCl_2\mathbf{L}_2$ keeps their solid state structures even in DMF solution. The *in vitro* cytotoxicity test of the Pd^{II} complexes is in progress.

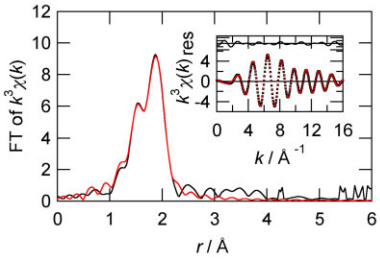


Figure 1 Fourier transforms and back-transforms (inset) of k^3-weighted EXAFS oscillations of $PdCl_2\mathbf{L}_2$ in solid state. Black and red denote observed and fitted data, respectively.

Table 1 Structural parameters of $PdCl_2\mathbf{L}_1$

	solid state		in DMF	
path	r / Å	$10^3\sigma$ / Å^2	r / Å	$10^3\sigma$ / Å^2
Pd–N	2.02(13)	4.8(7)	2.03(18)	5(11)
Pd–Cl	2.298(3)	3.1(3)	2.296(4)	3.3(4)
S_0^2	1.02(6)		1.05(8)	
R	0.027		0.027	

Table 2 Structural parameters of $PdCl_2\mathbf{L}_2$

	solid state		in DMF	
path	r / Å	$10^3\sigma$ / Å^2	r / Å	$10^3\sigma$ / Å^2
Pd–N	2.01(16)	4.8(8)	2.03(2)	5(12)
Pd–Cl	2.303(3)	3.1(4)	2.296(4)	3.0(5)
S_0^2	0.97(6)		1.01(9)	
R	0.022		0.019	

References

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