X-ray powder diffraction analysis of a new palladium(II) amino acid complex

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Powder X-ray diffraction data for a new palladium(II) amino acid complex, of composition $PdC_{12}H_{20}N_2O_4S_2$, are presented in this paper. Orthorhombic cell parameters are: $a = 10.740$ Å, $b = 19.999$ Å, and $c = 5.2470$ Å. © *2004 International Centre for Diffraction Data.*
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I. INTRODUCTION

Cisplatin, or cis-diamminedichloroplatinum(II), has been used for treatment of several human cancers, particularly testicular, ovarian, bladder, head and neck cancer (Jin and Ranford, 2000; Sohn *et al.*, 1997). The anticancer properties of cisplatin were first observed by Barnet Rosenberg at the Michigan State University in 1965, but only in 1978 was this compound approved worldwide for treatment of cancer (Lebwohl and Canetta, 1998). However toxic side effects of cisplatin, mainly nephrotoxicity, neurotoxicity (Sohn *et al.*, 1997) and also ototoxicity (Butour *et al.*, 1997) had limited its use and have led to the development of second generation drugs. The interest to develop new complexes with lower side effects but at the same time with high activity against tumors has stimulated the synthesis of many new complexes. So, new complexes of platinum(II) and their palladium(II) analogues have been prepared and studied as anticancer drugs. Recently, some complexes containing Pt(II) and Pd(II) with mixed ligands such as amino acids and 1,10-phenanthroline displayed some cytotoxic activities *in vitro* against *Molt-4*, a human leukaemia cell line (Jin and Ranford, 2000). By considering such observations, we prepared a new Pd(II) complex containing in its composition a sulfur amino acid, derived from garlic, and tested the activity of this complex against the proliferation of cancer cells. The preliminary results for the activity *in vitro* of this new Pd(II) complex, of composition $PdC_{12}H_{20}N_2O_4S_2$, showed its potent effect over *HeLa* tumorigenic cells derived from human cancer (Moreira *et al.*, 2003). Tests *in vivo* with mice and rats are currently in progress. The present work is dedicated to the X-ray characterization of the complex $PdC_{12}H_{20}N_2O_4S_2$ using the powder diffraction technique.

II. EXPERIMENTAL

Powder microcrystalline $PdC_{12}H_{20}N_2O_4S_2$ was obtained by reaction of Li_2PdCl_4 with the salt of the amino acid derived from garlic in methanol under stirring for 2 h. The fine yellow powder formed was filtered, washed with methanol, and dried under P_4O_{10} in a dessicator. Yield of the synthesis was about 70%. After trituration (mortar and pestle grinding), the Pd(II) complex was analyzed by using elemental analysis, powder X-ray diffractometry, and thermal analysis.

III. INSTRUMENTAL CONDITIONS

Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were performed by using a CHNS-O EA1110 Analyzer, CE Instruments; cysteine was used as a reference substance. Thermal analyses were performed on a Thermoanalyzer TGA/DTA simultaneous SDT 2960 TA Instruments in the following conditions: synthetic air, 100 cm^3/min and heating rate of 10 °C/min, from 40 to 900 °C. Powder X-ray analysis was performed on a D 5000 Siemens Diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) with a graphite diffracted beam monochromator. The sample was scanned over the 2θ range from 4° to 70° in 0.05° step. The counting time was 1.0 s/step.

IV. RESULTS AND DISCUSSION

Elemental analysis for C, H, N, and S in the palladium(II) complex are shown in Table I. According to the experimental data, the composition $PdC_{12}H_{20}N_2O_4S_2$ is proposed.

TABLE I. Elemental analysis for $PdC_{12}H_{20}N_2O_4S_2$.

Elements	Calculated (%)	Found (%)
C	33.8	32.8
H	4.70	4.80
N	6.60	6.40
S	15.0	14.7

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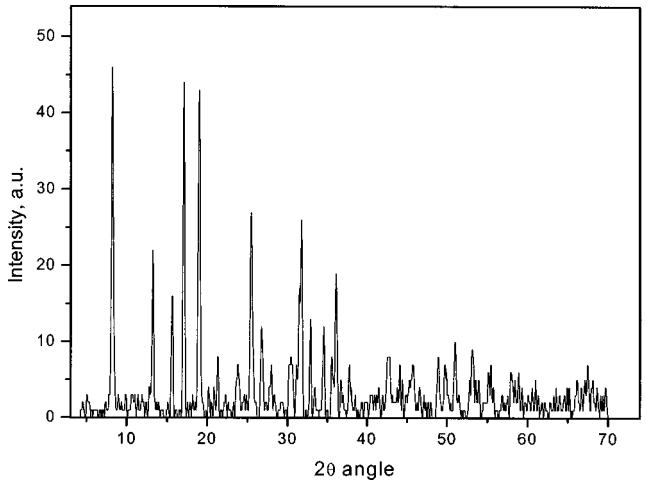

Figure 1. X-ray diffractogram of $PdC_{12}H_{20}N_2O_4S_2$.

TABLE II. X-ray diffractometry data $PdC_{12}H_{20}N_2O_4S_2$ (variation ±0.05 Å).

I/I_0	h	k	l	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)
100	1	0	0	10.74	10.74
48	0	3	0	6.670	6.666
35	1	3	0	5.649	5.664
95	2	1	0	5.183	5.186
92	0	2	1	4.666	4.646
08	1	2	1	4.254	4.264
17	0	3	1	4.159	4.123
06	0	5	0	3.989	4.000
15	1	5	0	3.730	3.748
59	2	2	1	3.494	3.514
26	0	6	0	3.327	3.333
15	1	6	0	3.186	3.183
18	3	1	1	2.929	2.925
58	0	6	1	2.815	2.184
29	1	6	1	2.720	2.722
09	3	5	0	2.678	2.668
26	4	2	0	2.591	2.593
41	4	3	0	2.487	2.491
11	1	7	1	2.446	2.443
15	1	3	2	2.381	2.381
06	1	9	0	2.175	2.176
18	3	0	2	2.111	2.116
15	4	5	1	2.051	2.052
10	2	5	2	2.037	2.031
15	5	1	1	1.981	1.978
18	4	1	2	1.860	1.868
16	4	7	1	1.831	1.833
21	6	0	0	1.788	1.790
20	0	2	3	1.723	1.723
12	4	9	0	1.711	1.712
11	1	11	1	1.697	1.696
13	2	0	3	1.663	1.663
16	5	1	2	1.655	1.657
07	2	9	2	1.618	1.617
14	0	10	2	1.590	1.591
13	3	1	3	1.567	1.567
10	7	2	0	1.517	1.517
12	7	4	1	1.411	1.413
16	5	11	0	1.387	1.388

Thermogravimetric analysis has been useful for confirmation of the complex composition as well as for identification of the final residue of the sample after thermal treatment. According to the thermogravimetric data the complex composition was confirmed as being equal to $PdC_{12}H_{20}N_2O_4S_2$. Ligand oxidation starts at a temperature near 200 °C. Residue composition, after oxidation of the Pd(II) complex, over 900 °C was identified by X-ray diffractometry as a mixture of PdO (Powder Diffraction File Database, 1994) and Pd (Powder Diffraction File Database, 1994). Palladium content in the $PdC_{12}H_{20}N_2O_4S_2$ was quantified by analyzing its thermogravimetric residue at 900 °C (calculated 24.9%; found 23.7%).

The powder X-ray diffractogram of $PdC_{12}H_{20}N_2O_4S_2$ is shown in Figure 1.

Indexing of the experimental X-ray powder diffraction data for $PdC_{12}H_{20}N_2O_4S_2$ was performed by considering the similarity of the X-ray data collected for this compound in comparison to the orthorhombic form of biotin (Powder Diffraction File Database, 1996). The known data for biotin permitted us to choose the primary cell parameters for $PdC_{12}H_{20}N_2O_4S_2$ which, after refining, by a least-squares approach, led to the following lattice parameters: $a = 10.740$ Å, $b = 19.999$ Å, and $c = 5.2470$ Å. The resulting indexation is shown in Table II.

V. CONCLUSION

The composition of the new Pd(II) amino acid complex, of formula $PdC_{12}H_{20}N_2O_4S_2$, was determined by elemental and thermogravimetric analyses. Thermal decomposition leads to PdO and Pd as final products. X-ray diffraction data for $PdC_{12}H_{20}N_2O_4S_2$ have been successfully indexed on an orthorhombic system with the following cell parameters: $a = 10.740$ Å, $b = 19.999$ Å, and $c = 5.2470$ Å.

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