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NMR and X-ray Studies of Pd(II) and Pt(II) Complexes with S-Methyl-L-cysteine Sulfoxide

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IR, NMR and X-ray studies have shown that in the Pt(II) or Pd(II)–S-methyl-L-cysteine sulfoxide (SOMC) complexes the ligand molecule coordinates to the metal ion via the sulfur and amine donors. Two isomers are found in solution which differ by the ligand conformation on the sulfur center. Crystals of dichloro-[(S-methyl-L-cysteine)sulfoxide] palladium(II) monohydrate are orthorhombic, space group $P2_12_12_1$ *with* a = *17.858(4),* b = *8.690(3),* c = *7.008 (2) Å and Z = 4. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations to a final R = 0.061 for 942 counter reflections. Coordination around palladium is slightly distorted square-planar and involves the sulfur and the nitrogen atoms of the amino acid molecule and two chlorine atoms. The five-membered chelate ring has a λ conformation. The R, S absolute configuration of the ligand is confirmed in this study. Only one of the SOMC–Pd isomers was found to be present in the studied crystals.*

Introduction

Our recent studies of Pd(II) and Pt(II) complexes with sulfur containing amino acids [1–3] have suggested that two donor groups *i.e.* S and NH_2 or COO^- may be involved in the coordination. In each case few species were formed and their identification has caused some difficulties [1, 2]. The differences between the complex species created in solution have derived from various conformations and coordination sites [1–3]. The sulfur atom was the most effective donor for both Pd(II) and Pt(II) ions at any pH. Beside the thioetheric group, the nitrogen donor seemed to be more reactive than the carboxyl one in the complexation of the metal ions [2, 3]. To get more results about the sulfur donation and the possible inversion on the sulfur atom in S-methyl-L-cysteine (SMC) and its derivatives, the Pd(II) and Pt(II) complex formations with the S-methyl-L-cysteine sulfoxide were also studied. In this ligand, the sp^3 orbitals of the sulfur atom are involved in two σ bonds with carbons and in one sulfur–oxygen σ bond. There is still a fourth sp^3 hybrid with a lone electron pair which may be used to create the metal–sulfur bond during the Pd(II) and Pt(II) complex formation.

In this report, we present the NMR, IR and X-ray data for some Pd(II) and Pt(II) complexes with S-methyl-L-cysteine sulfoxide (SOMC).

Experimental

SOMC was prepared from SMC received from Fluka. 4 g of SMC was dissolved in 60 ml of acetic acid. 3.5 ml of H_2O_2 was added to the mixture, then it was left during 4 hr at 12 °C. The solution was distilled under reduced pressure. 50 ml of acetone were added to the distillate and the sample was left to the next day. The obtained precipitate was filtered and dried. The formed ligands have been recrystallized from water–ethanol solution (m.p. 162 °C).

K_2PtCl_4 was used as received from Fluka. K_2PdCl_4 was obtained by crystallization of KCl and $PdCl_2$ solutions containing HCl.

NMR studies were performed in D_2O solution with ligand concentration equal to 0.2 *M*.

^1H and ^{13}C NMR spectra were recorded on a JEOL 100 MHz JMN-PS-100 spectrometer, using tert-butyl alcohol and dioxane as internal standards. All NMR spectra were measured at 25 ± 2 °C. For dynamic studies, the temperature was increased up to 96 °C and adjusted by the JES-VT3 unit. Analysis of the proton ABC spectra was carried out on a JEC-6 computer.

Data of X-ray intensities were collected on a Syntex $P2_1$ computer controlled four-circle diffracto-

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TABLE I. ^1H NMR Parameters of SOMC–Metal Free Ligand and SOMC–Me(II) Solution Spectra as a Function of pH. $\nu = 0$ for tBuOH. Me = Pd and Pt. Chemical shifts are given in Hz.

Compound	pH		ν_A	ν_B	ν_C	ν_{CH_3}	$\nu_{^{195}Pt-H}$	$\lvert J_{AB}\rvert$	J_{AC}	J_{BC}	p_I	p_{II}	p_{III}
SOMC	0.8	(1)[b]	212.2	232.4	334.4	160.2		13.8	6.8	5.5	0.26	0.38	0.36
		(2)	222.9	227.1	332.7			14.0	5.9	6.0	0.31	0.30	0.39
	4.7	(1)	197.6	221.0	292.4	157.3		13.5	7.6	5.8	0.29	0.45	0.26
		(2)	211.7	215.8	298.0			14.2	5.1	6.4	0.33	0.27	0.40
	7.2	(1)	197.1	218.3	289.5	156.2		13.5	7.8	5.5	0.29	0.47	0.24
		(2)	207.9	210.7	292.0			14.2	5.6	6.2	0.33	0.27	0.40
	12.6	(1)	173.1	193.7	236.8	149.3		12.9	9.8	3.0	0.04	0.65	0.31
		(2)	182.9	194.7	236.3			13.1	6.0	6.9	0.39	0.31	0.30
SOMC–Pd													
1:1	1.1	(1)	?[a]	?	?	234.4							
		(2)	?	?	?	241.8							
	4.3	(1)	?	?	?	227.5							
		(2)	?	?	?	237.7							
SOMC–Pt													
1:1	1.4	(1)	?	?	?	241.4	25.4						
		(2)	?	?	?	247.6	24.6						
	3.9	(1)	?	?	?	237.3	24.7						
		(2)	?	?	?	245.4	25.6						

[a] The ABC spectra analysis was not possible because of the poor spectra resolution. [b] (1) and (2): labels of two diastereoisomers.

meter equipped with a scintillation counter and graphite monochromator.

Infrared spectra of D_2O solutions were recorded on a Perkin-Elmer model 621 spectrometer. The pH was adjusted with KOH in D_2O and HNO_3 and measured on a Mera-Elmat N-512 pH meter.

Spectroscopic Methods in Solution

NMR Results for SOMC Metal-free Ligand

^1H NMR spectra of the metal-free SOMC have shown that two different species are present in solution at the whole studied pH range. Two ABC multiplets corresponding to αCH–βCH$_2$ proton unit are observed but only one resonance appears for the methyl (SCH_3) protons (Table I, Fig. 1). Both ABC sets of lines are almost equal in intensity but their ^1H NMR parameters are different (Table I). The rotamer populations around the C_α–C_β bond were calculated according to Pachler's approximation [4] for the rotamer notation given in Fig. 2.

In comparison to the proton chemical shifts of SMC, those of SOMC are significantly downfield shifted because of the sulfur–oxygen double bond formation. The presence of the latter bond causes also the existence of an asymmetric center on the sulfur atom, which was not the case in the SMC molecule. Thus, the two ^1H NMR spectra observed for the metal-free ligand derive from two diastereoisomers which differ from each other on the sulfur asymmetric center.

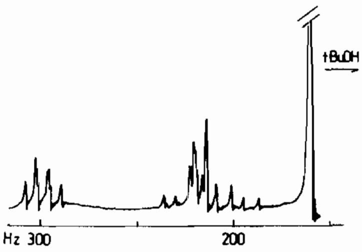
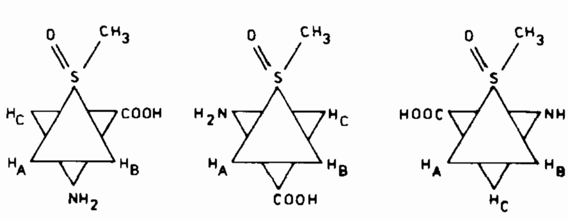


Fig. 1. ^1H NMR spectrum for SOMC free ligands.



I II III

Fig. 2. Rotamer notation of the SOMC molecule.

TABLE II. ^{13}C NMR Chemical Shifts of SOMC–Me(II) Complexes in D_2O Solutions are Given in ppm Relative to Dioxane. Me = Pd and Pt.

Compound	pH		ν_{COO^-}	ν_C	ν_C	ν_{SCH_3}
SOMC	1.1	(1)[b]	−103.4	15.3	17.9	29.4
		(2)	−105.1	14.6	17.2	28.5
	3.1	(1)	−104.7	14.4	16.5	29.3
		(2)		13.7	15.8	28.4
SOMC–Pd						
1:1	1.1	(1)	−102.8	2.2	11.2	23.2
		(2)		2.6	12.0	23.8
	3.0	(1)	−104.6	1.0	10.3	23.8
		(2)		1.5	9.8	23.2
2:1	3.0	(1)	−104.4	*[a]	10.3	23.2
		(2)		*	9.7	24.1
SOMC–Pt						
1:1	3.2	(1)	−104.2	2.3	7.8	23.5
		(2)		3.0	8.4	24.1

[a] *cannot be distinguished from the spectrum. [b] (1) and (2) are labels of two diastereoisomers.

The ^{13}C NMR spectra of the SOMC molecule consist of two sets of resonances for each carbon (Table II). The double resonance of the COO^- group becomes a singlet line at pH above 3.

NMR and IR Analysis of the SOMC–M(II) Solution Spectra (M = Pd and Pt)

In the ^1H NMR spectra of the 1:1 SOMC–M(II) solutions (M = Pd and Pt), two superposed ABC spectra and two methyl SCH_3 resonances are observed with an intensity ratio nearly equal to 1. For the Pt(II)-containing solutions, two additive doublets appear on the spectra corresponding to the additional splitting of the SCH_3 resonances by the ^{195}Pt nuclei (Table I). In the pH region 1–4 for both 1:1 Pd(II) and Pt(II)–SOMC containing solutions, there are very remarkable downfield shifts of the SCH_3 proton resonances equal to 0.70–0.80 ppm compared to the free ligand (Table I). This suggests the sulfur donor coordination to Pd(II) and Pt(II) ions [1]. The ABC spectra analysis was impossible as the αCH–βCH_2 proton unit spectra were not resolved enough. The ^{13}C NMR spectra of the 1:1 SOMC–M(II) solution present two sets of SOMC carbon resonances of nearly equal intensity. The low field chemical shifts upon the Pd(II) coordination to the SOMC molecule are equal to 12.2–13.4 ppm for the α carbon, 5.5–6.7 ppm for β carbon and 4.3–6.1 ppm for the SCH_3 carbon. The chemical shift of the COO^- carbon is almost unchanged (0.1 ppm). The chemical shift changes upon the Pt(II) coordination to the SOMC molecule are very close to those found with the Pd(II) ions (Table II). The variations on the SCH_3 carbon resonance strongly suggest that in both chemical species found for Pd(II) and Pt(II) ions, the metal ion is bound to the sulfur donor. The slight changes on the ν_{COO^-} upon the metal ion coordination excludes the involvement of this group in metal ion binding. Thus, the considerable downfield shift of the ν_{C_α} may derive only from the SOMC coordination to Pd(II) and Pt(II) metal ion via the NH_2 group.

It should be mentioned that there is no coalescence of two present 1:1 complex spectra during the heating of the solutions up to 96 °C as was the case for Pd–SMC solutions [1].

NMR spectra analysis of the 1:2 molar ratio metal SOMC solutions in pH 1–10 does not show any major formation of 1:2 M(II)–SOMC complexes. IR spectra of D_2O solutions of metal-free SOMC at pH range 1–6 show two bands corresponding to asymmetric stretching vibrations of protonated (1730 cm^{-1}) and unprotonated (1627 cm^{-1}) carboxyl group. After addition of Pd(II) and Pt(II) ions to the SOMC-containing solution, these two bands appear at 1720 cm^{-1} and 1620 cm^{-1} for the same pH region. Thus, the IR method also strongly suggests that the carboxyl group remains uncoordinated as the asymmetric stretching vibration band for the COO–M(II) unit should occur at about 1640 cm^{-1} (M = Pd and Pt) [2].

Crystal Structure

Structure Determination

Crystals of dichloro[(S-methyl-L-cysteine)sulfoxide]palladium(II) monohydrate are orthorhombic, space group $P2_12_12_1$, a = 17.858(4), b = 8.690(3), c = 7.008(2) Å, Z = 4, $\mu(CuK_\alpha, \lambda = 1.5418$ Å) = 204.8 cm^{-1}. Intensities from a crystal 0.09 × 0.08 × 0.11 mm were collected using graphite-monochromatized CuK_α radiation on a Syntex $P2_1$ diffractometer with an θ–2θ scan. 942 reflections with $I > 1.96\ \sigma(I)$ were used in the structure determination. The data were corrected for Lorentz and polarization effects only.

The structure was solved by heavy-atom method and refined by full-matrix least-squares technique. A final full-matrix refinement including the non-hydrogen atoms with anisotropic temperature factors and the H atoms with fixed positional and thermal parameters (B = 3.0 Å^2) converged at R = 0.061 and R_w = 0.075. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion corrections were obtained from International Tables for X-ray Crystallography (1974) [5].

All calculations were performed with the Syntex XTL structure determination system (NOVA 1200 computer and additional external disc memory).

TABLE III. Final Fractional Atomic Coordinates, with e.s.d.s in Parentheses of Non-hydrogen Atoms.

	x	y	z
Pd	0.14326(9)	0.01912(15)	0.14985(22)
Cl(1)	0.2300(3)	0.1148(7)	−0.0639(8)
Cl(2)	0.1142(4)	−0.1904(6)	−0.0356(9)
S	0.0629(3)	−0.0557(5)	0.3689(8)
O(1)	−0.0180(7)	−0.0365(19)	0.3194(22)
O(2)	0.1864(9)	0.4251(18)	0.5936(24)
O(3)	0.0923(8)	0.3455(18)	0.7780(21)
O(4)	0.1666(7)	0.4737(17)	0.0602(21)
N	0.1619(9)	0.2057(18)	0.3156(23)
C(1)	0.1344(14)	0.3424(23)	0.6235(32)
C(2)	0.1071(12)	0.2249(22)	0.4787(35)
C(3)	0.0870(12)	0.0719(24)	0.5640(30)
C(4)	0.0777(12)	−0.2449(24)	0.4604(33)

TABLE V. Calculated Positions of the H Atoms (B = 3.0 Å^2).

	x	y	z
H(1)	0.043	−0.252	0.570
H(2)	0.059	0.266	0.420
H(3)	0.054	−0.296	0.347
H(4)	0.128	−0.281	0.500
H(5)	0.110	0.446	0.871
H(31)	0.043	0.084	0.655
H(32)	0.130	0.031	0.641
H(N1)	0.161	0.301	0.233
H(N2)	0.214	0.197	0.373

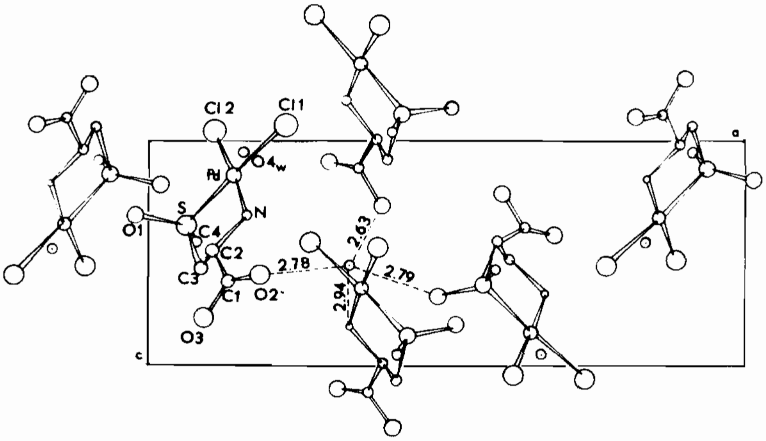


Fig. 3. Projection of the structure of PdCl$_2$(SOMC)·H$_2$O along *b*-axis.

TABLE IV. Final Anisotropic Temperature Factors of Non-hydrogen Atoms. The anisotropic temperature factor is of the form $\exp[-(1/4)(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	2.07(6)	1.84(5)	2.12(6)	0.25(6)	0.05(6)	−0.09(6)
Cl(1)	2.3(2)	4.3(3)	3.2(2)	0.5(2)	0.9(2)	0.1(2)
Cl(2)	7.0(4)	2.3(2)	3.1(3)	0.0(3)	−0.6(3)	−0.5(2)
S	2.1(2)	1.8(2)	2.6(2)	−0.2(2)	−0.2(2)	−0.2(2)
O(1)	1.2(6)	5.6(9)	3.9(8)	0.2(6)	−1.6(6)	−0.3(8)
O(2)	3.7(8)	3.8(8)	4.4(9)	−2.06(7)	1.3(7)	−1.6(7)
O(3)	2.7(7)	3.1(7)	3.1(7)	−0.0(6)	0.9(6)	−0.9(6)
O(4)	2.1(6)	2.8(6)	3.2(6)	−0.0(6)	−0.3(5)	0.4(6)
N	1.9(8)	1.9(6)	2.0(8)	−0.5(6)	1.0(7)	−0.9(6)
C(1)	3.6(12)	1.8(8)	2.4(10)	0.4(10)	0.1(11)	−0.3(8)
C(2)	1.5(9)	1.4(9)	2.7(11)	0.5(8)	−0.9(9)	0.4(8)
C(3)	2.2(9)	2.2(9)	2.0(8)	0.3(8)	−0.6(8)	0.7(8)
C(4)	2.3(11)	1.8(8)	2.5(11)	−0.6(8)	−0.3(9)	0.1(8)

TABLE VI. A Comparison of Bond Lengths (Å) and Angles (°) Obtained from Relevant Compounds.

	$PdCl_2(SMC)$* [8]		$PdCl_2(SOMC)$	$PtCl_2(SOMC)$ [11]	SOMC [7]	$PdCl_2(MetH)$ [9]	$PtCl_2(MetSO)$ [10]
	I	II					
$M{-}Cl_{trans\,S}$	2.324(3)	2.312(7)	2.310(6)	2.292(4)		2.332(4)	2.323(2)
$M{-}Cl_{trans\,N}$	2.307(4)	2.305(4)	2.296(6)	2.299(4)		2.308(4)	2.304(2)
M–S	2.230(4)	2.261(4)	2.200(6)	2.182(3)		2.265(4)	2.198(2)
M–N	2.050(9)	2.044(10)	2.022(16)	2.046(12)		2.061(14)	2.063(7)
S–O			1.496(14)	1.494(11)	1.488(12)		1.442(7)
$S{-}C_{met}$	1.81(2)	1.83(2)	1.78(2)	1.75(1)	1.81(2)	1.80(2)	1.78(1)
$S{-}C_\beta$	1.83(2)	1.85(1)	1.81(2)	1.78(1)	1.83(2)	1.83(2)	1.78(1)
$C_\alpha{-}C_\beta$	1.58(2)	1.55(2)	1.50(3)	1.50(2)	1.49(3)	1.49(2)	1.53(1)
$C_\alpha{-}N$	1.46(2)	1.47(2)	1.51(3)	1.45(2)	1.51(2)	1.47(2)	1.48(1)
$C_\alpha{-}C$	1.50(2)	1.53(2)	1.52(3)	1.50(2)	1.57(3)	1.54(2)	1.47(1)
C–O	1.18(2)	1.16(2)	1.19(3)	1.23(2)	1.21(2)	1.20(2)	1.23(1)
C–OH	1.34(2)	1.34(2)	1.32(3)	1.32(2)	1.24(2)	1.30(2)	1.33(1)
Cl(1)–M–Cl(2)	92.5(2)	92.5(3)	94.0(2)	90.6(2)		92.5(2)	90.8(1)
S–M–N	87.2(3)	86.8(5)	86.8(5)	86.3(3)		96.9(4)	93.7(2)
Cl–M–S	87.5(5)	89.4(3)	90.8(2)	93.5(1)		85.2(2)	90.9(1)
Cl–M–N	92.5(5)	91.3(6)	88.5(5)	89.5(3)		85.3(4)	84.8(2)
M–S–O			115.8(6)	117.9(4)			116.1(3)
$M{-}S{-}C_{met}$	107.3(9)	107.2(9)	115.3(8)	114.2(5)		110.2(5)	112.4(4)
$M{-}S{-}C_\beta$	100.2(8)	98.3(7)	101.0(7)	102.2(5)		104.5(8)	108.2(3)
$O{-}S{-}C_{met}$			109.2(10)	108.8(7)	107.5(7)		108.9(5)
$O{-}S{-}C_\beta$			109.6(9)	109.6(7)	104.4(8)		109.7(5)
$C_\beta{-}S{-}C_{met}$	104.2(13)	99.7(13)	104.9(10)	102.7(7)	96.7(10)	100.1(9)	100.3(5)
M–N–C	113.1(11)	111.8(12)	114.5(12)	112.2(9)		123.9(10)	123.2(6)
$S{-}C_\beta{-}C_\alpha$	106.8(13)	103.4(13)	107.3(15)	109.1(10)	114.9(14)	117.0(12)	111.9(7)
$C_\beta{-}C_\alpha{-}N$	111.6(17)	110.9(18)	111.0(17)	111.7(12)	109.3(13)	108.0(13)	111.8(7)

*Includes two crystallographically independent molecules.

Final positional and thermal parameters are given in Tables III–V. The calculated bond lengths and angles are shown in Table VI. Figure 3 shows the projection of the crystal structure on the (010) plane and indicates the numbering system used. The absolute configuration of the molecule was assigned as R(C2)-S(S) with reference to the known configurations of L-cysteine [6] and S-methyl-L-cysteine sulfoxide [7].

Description and Discussion of the Structure

The results of the structure analysis of dichloro-[(S-methyl-L-cysteine sulfoxide)] palladium(II) monohydrate show that SOMC behaves as a bidentate ligand coordinating through sulfur and nitrogen to palladium, forming a five-membered chelate ring. The square-planar coordination around palladium is completed by chlorine atoms (Pd is situated closely on the Cl(1)Cl(2)NS plane – Table VII). The same type of coordination has been found in the crystal structures of an analogous palladium(II) complex with S-methyl-L-cysteine [8], dichloro (RS-methionine) palladium(II) [9], dichloro[(2S,SR)-methionine sulfoxide] platinum(II) hydrate [10] and dichloro[(2S,SR)-S-methylcysteine sulfoxide] platinum (II) hydrate [11].

The bond lengths and angles in $PdCl_2(SOMC)\cdot H_2O$ compare closely with those of the related complexes cited above (Table VI). The strengthening of sulfur–metal bond caused by the presence of the oxygen atom was observed also in the case of Pt(II)-S-methylcysteine sulfoxide [11] and Pt(II)–methionine sulfoxide complex [10]. The other interatomic distances and bond angles of $PdCl_2(SOMC)\cdot H_2O$ are in good agreement with the values obtained for S-methyl-L-cysteine sulfoxide ligand [7] and other comparable sulfoxides and amino-acids.

The carboxylic group is planar and protonated. The two C–O lengths corresponding to C=O and C–OH bonds are 1.19 and 1.32 Å respectively. The nitrogen atom is 0.22 Å out of the $C_\alpha COO$ plane. The C_α and C_β are situated on opposite sides of the plane PdSN at 0.25 and –0.42 Å, respectively.

The chelate ring is in the λ conformation with an equatorial orientation of the carboxylic group. The angles formed by the -COOH, $S\text{-}CH_3$ and S-oxide substituents with the plane of coordination of the chelate ring PdSN are 12.1, 46.9 and 60.6°. The analogous angles in related complex Pt(2S,SR)-S-methylcysteine sulfoxide)Cl_2 [11] are: –COOH, 27.9; $S{-}CH_3$, 57.8; S–oxide, 51.0°. The S-methyl-L-cysteine

TABLE VII. Least-squares Planes. Deviations (Å) of relevant atoms from the planes and their e.s.d. are given in parentheses.

Plane 1 through *Cl(1), Cl(2), S, N*

$-0.7217X + 0.5218Y - 0.4547Z + 2.2319 = 0$

Cl(1) −0.009(6), Cl(2) 0.010(7), S −0.007(5), N 0.072(16), Pd −0.0054(15)

Plane 2 through *Pd, S, N*

$-0.7306X + 0.4905Y - 0.4751Z + 2.2865 = 0$

Cl(1) – 0.012(6), Cl(2) 0.103(7), O(1) 1.303(14), O(2) – 0.310(16), O(3) −0.03(15)
C(1) −0.08(2), C(2) 0.25(2), C(3) −0.42(2), C(4) – 1.30(2), H(2) 1.25

Plane 3 through *Pd, Cl(1), Cl(2)*

$-0.7197X + 0.5274Y - 0.4516Z + 2.2278 = 0$

S −0.004(5), N 0.091(16)

Plane 4 through *C(1), O(2), O(3)*

$-0.6096X + 0.6597Y - 0.4395Z + 1.4203 = 0$

Plane 5 through *C(2), C(1), O(2), O(3)*

$-0.6009X + 0.6818Y - 0.4172Z + 1.2204 = 0$

C(1) −0.016(22), C(2) 0.004(21), O(2) 0.003(16), O(3) 0.002(15), N −0.221(16)

Interplanar angles (°)

1–2	2.2	2–3	2.6
1–3	0.4	2–4	12.1
1–4	10.2	3–4	9.9
1–5	11.7		

sulfoxide molecule has two asymmetric centers, C_α and sulfur atom. The X-ray diffraction study of the $PdCl_2(SOMC)\cdot H_2O$ complex established that chiral centers have the R and S configurations, respectively.

The conformation of the molecule is described by torsion angles φ_1, φ_2 and χ, defined in [12].

	φ_1	φ_2	χ
Dichloro-S-methyl-L-cysteine sulfoxide Pd(II)	11.1(22)	−171.6(18)	−48.5(18)
Dichloro-S-methyl-L-cysteine Pd(II)	7.5	−174.4	−52.5
	−10.5	168.7	−60.0
Dichloro-S-methylcysteine sulfoxide Pt(II)	2.7	179.0	45.9
S-methyl-L-cysteine sulfoxide	−3.2	170.5	−65.1

The values of these angles are in good agreement with those calculated for the $Pd(SMC)Cl_2$ and $Pt(SOMC)Cl_2$ complexes and for uncomplexed S-methyl-L-cysteine sulfoxide. The differences in the torsion angles are attributable to hydrogen bonding and molecular packing forces. Conformational changes φ produce change in nonbonded interactions between carboxyl group, and nitrogen and C_β atoms of the side chain. In $Pd(SOMC)Cl_2$ complex O(2)....N and O(3)....C(3) contact distances are 2.76 and 2.81 Å, respectively.

The molecular packing viewed down *b* is shown in Fig. 3. The structure consists of discrete, square-planar molecules of the $Pd(SOMC)Cl_2$ hydrogen bonded through the water of crystallization O(4). Packing contacts which can be considered as possible hydrogen bonds are shown in Fig. 3.

On the basis of the preliminary X-ray studies, it was proved that the crystals of the 1:1 molar ratio SOMC–Pt(II) complex are isomorphic to the SOMC–Pd(II) crystals.

An interesting difference between SOMC–Pd(II) and SOMC–Pt(II) complexes was observed when their crystals were dissolved in aqueous solution. In the case of SOMC–Pd(II)Cl_2 complex, the ^1H NMR spectra of the dissolved crystals are exactly the same as those obtained for a freshly prepared 1:1 SOMC–Pd(II) solution. For the Pt(II) complex crystals, only one isomer could be observed in the ^1H NMR spectra. The spectrum of the second isomer appears after 3 days. This confirms that only one ligand is bound to metal and that two isomers may be created by an inversion on the sulfur atom, which does not involve a lone electron pair in its mechanism [13, 14].

Conclusion

IR and NMR solution studies as well as X-ray crystal investigations have shown that sulfur-containing amino acids use only two donors in the coordination to Pd(II) and Pt(II) metal ions, *i.e.* S and NH_2. Thus, the different species observed in solution come from different conformations of the ligand, especially on the asymmetric sulfur center. The solid state Pt(II) complex is found to be appropriate to separate two ligand diastereoisomers, which is of great importance in the synthesis of SOMC.

The presence of the S=O double bond hinders the dynamic process of inversion on the sulfur with the use of a lone electron pair. That is why no exchange process is observed in the ^1H NMR spectra in Pd–SOMC system when the temperature was increasing. The results for the dissolved SOMC–Pd(II)Cl_2 and SOMC–Pt(II)Cl_2 crystals suggest that the inversion process on sulfur may proceed with binding of solvent molecules in intermediate reactions.

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