The superstructure

The anion possesses an approximate centre of inversion which is situated near $\frac{1}{2},\frac{1}{4},\frac{1}{2}$. Together with the crystallographic centre at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ this results in an apparent translation of the anion by $b/2$ (Fig. 1). Furthermore, the two independent $[N(CH_3)_4]^+$ cations are also situated as if repeated by $b/2$. However, the $Na-H_2O$ arrangement is not repeated in this way, even if some individual atoms may be considered to be. This may be explained by the protonation of the anions, with the H atom pointing alternately in the $-x$ and $+x$ directions for anions at y and $y+\frac{1}{2}$, respectively. The conditions for Na^+ coordination to the arsenate O atoms are thus different, with the given result. The number of reflexions with $I > 3\sigma(I)$ [$I > 2\sigma(I)$] was 3558 [3777] for k even and 1401 [1898] for k odd. The intensity was $<10\sigma(I)$ for 75% of the k odd reflexions and the maximum value was $55\sigma(I)$.

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X-ray and NMR Studies of the Interaction Between Pd^{II} and *S*-Methyl-L-cysteine Methyl Ester

BY M. KUBIAK, A. ALLAIN*, B. JEŻOWSKA-TRZEBIATOWSKA, T. GŁOWIAK AND H. KOZŁOWSKI

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

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Abstract

Both X-ray and NMR results indicated that *S*-methyl-L-cysteine methyl ester (SmcOMe) is coordinated to Pd^{II} through the S and N donors. X-ray studies were performed on crystals of the 1:1 ligand–metal complex. Crystals of dichloro(*S*-methyl-L-cysteine methyl ester)palladium(II) monohydrate are tetragonal, space group $P4_12_12$, with $a = b = 8{\cdot}309\,(3)$, $c = 33{\cdot}860\,(9)$ Å, $Z = 8$. The structure was refined to $R = 0{\cdot}062$ for 823 counter reflections. The coordination around Pd is slightly distorted square planar and involves the S and N atoms of the amino acid molecule and two Cl atoms. The five-membered chelate ring has an envelope-like conformation. The absolute configuration of the ligand was assigned as (3*R*,S*R*) with reference to the known *R* configuration of L-cysteine.

* Present address: Institut de Chimie, Université L. Pasteur, 4 rue B. Pascal, 67000 Strasbourg, France.

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Introduction

NMR studies on the interactions of Pd^{II} and Pt^{II} ions with *S*-methyl-L-cysteine and its derivatives in aqueous solution usually show the existence of several species in equilibrium in any pH range (Jeżowska-Trzebiatowska, Allain & Kozłowski, 1977, 1979; Allain, Kubiak, Jeżowska-Trzebiatowska, Kozłowski & Głowiak, 1980). *S*-Methyl-L-cysteine (Smc) and its sulfoxide analog (SOmc) may use more than two coordination sites to bind the metal ion. Thus, the presence of several chemical species in Pd^{II}– or Pt^{II}–Smc(SOmc)-containing solutions could be due to different coordination sites used by the ligand in the metal-ion binding. IR (Jeżowska-Trzebiatowska *et al.*, 1979) and X-ray studies (Battaglia, Corradi, Palmieri, Nardelli & Tani, 1973; Allain *et al.*, 1980) have shown, however, that the different NMR spectra have their origin in the different conformation of the ligand bound to the metal ion *via* S and N donors. *S*-Methyl-L-cysteine methyl ester (SmcOMe) can use only two coordination sites to bind Pd^{II} or Pt^{II}, as the carboxyl group is blocked during the esterification process. Thus NMR and X-ray studies of the Pd^{II}–SmcOMe system should clarify the interpretation of our earlier NMR studies on metal–Smc and –SOmc systems (Jeżowska-Trzebiatowska *et al.*, 1977, 1979; Allain *et al.*, 1980).

Experimental

Crystals of $[PdCl_2(SmcOMe)].H_2O$ were prepared by the direct reaction of the ligand with aqueous $K_2[PdCl_4]$. SmcOMe was prepared by esterification of Smc (obtained from Fluka). 3 g of Smc was added to 30 ml of methanol. The mixture was cooled at 263 K and stirred. Drops of $SOCl_2$ were added to the mixture to the stoichiometric quantity. The solution was left for 48 h at room temperature. 60 ml of diethyl ether was added and the ester crystallized. Recrystallization was carried out from a mixture of methanol and diethyl ether.

NMR studies were performed in D_2O for the proton nuclei and in deuterated Me_2SO for the ^{13}C nuclei. ^1H and ^{13}C NMR spectra were recorded on a Jeol 100 MHz JMN-PS-100 spectrometer, with *tert*-butyl alcohol and dioxane as internal standards. All NMR spectra were measured at 298 ± 2 K. For dynamic studies, the temperature was increased to 369 K and adjusted by the JES-VT3 unit. The pH was adjusted with KOH in D_2O and HNO_3 in aqueous solution and measured on a Merat–Elmat N512 pH-meter.

The 1:1 Pd^{II}–SmcOMe *system in solution*

The 1:1 Pd^{II}–SmcOMe system was studied in D_2O solution up to pH 3. The complex concentration was very low because of the instantaneous formation of crystals in this pH range. At pH > 3, hydrolysis of the ester bound in the complex occurs and the ^1H NMR spectra present mainly the methanol resonance form. At pH < 3, the ^1H NMR spectra are composed of two sets of lines which are analogous to those of the 1:1 Pd^{II}–Smc solutions. The two superposed spectra have a line intensity ratio of 1:2. There is a remarkable downfield shift of the SCH_3 resonances compared to that of the metal-free ligand (from 0·896 to 1·464 and 1·414 p.p.m.), which confirms the S–Pd^{II} bond formation also in solution (Jeżowska-Trzebiatowska *et al.*, 1977, 1979).

Besides these two SCH_3 resonances there is a superposition of two *ABC* spectra which are not clear enough for analysis because of the low complex concentration in D_2O. The small downfield shifting of two OCH_3 resonances compared to that of metal-free SmcOMe from 2·591 p.p.m. to 2·633 and to 2·644 p.p.m. confirms the coordination of the amino group found by X-ray studies (see below). When the temperature increases the double resonances of the SCH_3 as well as the OCH_3 protons collapse at 347 K, *i.e.* at a temperature close to that found in the Pd^{II}–Smc system (Jeżowska-Trzebiatowska *et al.*, 1977).

The ^{13}C NMR spectra of the 1:1 SmcOMe system in deuterated Me_2SO consist of double carbon resonances for SCH_3, OCH_3 and C_β carbons and single resonances for C_α and carboxyl C atoms (Table 1). The SCH_3, C_β and C_α carbon resonances are shifted downfield compared to those of SmcOMe, *i.e.* 5·0 and 7·4 for SCH_3, 8·6 for C_β and 8·3 p.p.m. for C_α. Only minor changes are observed in the carboxyl and OCH_3 carbon resonances. Such results are in agreement with the S,N coordination of SmcOMe to Pd^{II}.

The two species found in solution correspond to two diastereoisomers, where SmcOMe is S,N coordinated to the metal ion, and differ from each other in the ligand conformation at the S-atom asymmetric center. The SCH_3 group may be *cis* or *trans* to the $COOCH_3$ group relative to the chelate ring (Jeżowska-Trzebiatowska *et al.*, 1979; Allain *et al.*, 1980; Battaglia *et al.*, 1973; Erickson, McDonald, Howie & Clow, 1968). Thus, the exchange process observed with increase of temperature corresponds to inversion at the

Table 1. ^{13}C NMR *chemical shifts of* Pd^{II}–SmcOMe *complexes in p.p.m. relative to dioxane, in deuterated* Me_2SO

	ν_{COOMe}	ν_{C_α}	ν_{C_β}	ν_{SCH_3}	ν_{OCH_3}
SmcOMe	−102·3	14·8	33·0	51·0	13·5
Pd^{II}–SmcOMe (1:1)	−102·0	6·5	*	46·0	13·6
			24·4	43·6	13·3

* Cannot be distinguished from the spectrum.

S atom, which proceeds *via* the lone-electron-pair mechanism on S (Haake & Turley, 1967; Turley & Haake, 1967; Cross, Green, Keat & Paterson, 1975).

Crystal structure

Structure determination

Crystals of dichloro(*S*-methyl-L-cysteine methyl ester)palladium(II) monohydrate, $[Pd(C_5H_{11}NO_2S)Cl_2].H_2O$, are tetragonal, $a = b = 8{\cdot}309$ (3), $c = 33{\cdot}860$ (9) Å; $M_r = 344{\cdot}5$, $D_c = 1{\cdot}96$ Mg m^{-3} for $Z = 8$; $\mu = 18{\cdot}88$ mm^{-1} for Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å); space group $P4_12_12$.

Crystals were obtained as dark-yellow plates. Preliminary oscillation and Weissenberg photographs indicated a tetragonal lattice and narrowed the choice of space group to one of the two enantiomers, $P4_12_12$ or $P4_32_12$. The cell parameters were determined by least-squares refinement from the setting angles of 15 reflections given by the automatic centering program.

All measurements for a crystal $0{\cdot}15 \times 0{\cdot}15 \times 0{\cdot}10$ mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and graphite monochromator. 887 independent reflections were measured up to $2\theta = 110°$ with the θ–2θ scan technique. The intensity of one periodically monitored reflection displayed no observable trend. The data were corrected for Lorentz and polarization effects. 832 reflections with $I > 1{\cdot}96\sigma(I)$ were used for the structure determination. All calculations were performed with the Syntex *XTL* structure determination system. Neutral-atom scattering factors and anomalous-dispersion corrections for Pd, Cl, S, O and N were obtained from *International Tables for X-ray Crystallography* (1974).

The structure was solved by the heavy-atom method and refined by full-matrix least squares in space group $P4_12_12$. A final full-matrix refinement including the non-hydrogen atoms with anisotropic temperature factors and H atoms with fixed coordinates (calculated for idealized positions) and thermal parameters ($B = 3{\cdot}0$ Å^2) converged at $R = 0{\cdot}062$ and $R_w = 0{\cdot}062$ for 823 reflections, where $w = 1/\sigma^2(F)$.

The absolute configuration of the molecule was assigned as (3*R*,S*R*) and is consistent with the known *R* configuration of L-cysteine (Harding & Long, 1968).

Final positional parameters are given in Table 2,* bond lengths and angles in Table 3. Fig. 1 shows the projection of the crystal structure on the (010) plane and indicates the numbering system.

* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35332 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	*y*	*z*	B_{eq}
Pd	0·13061 (18)	0·17706 (17)	0·38318 (5)	1·82
Cl(1)	0·1640 (7)	0·4512 (6)	0·3733 (2)	3·5
Cl(2)	0·0574 (7)	0·2034 (7)	0·4484 (2)	3·2
S	0·1079 (6)	−0·0928 (6)	0·3881 (2)	2·4
O(1)	0·2743 (21)	0·0170 (20)	0·2524 (4)	3·9
O(2)	0·4568 (22)	−0·1568 (23)	0·2785 (4)	4·8
O(3)	0·3892 (23)	0·4249 (31)	0·4585 (7)	9·2
N	0·1990 (20)	0·1400 (20)	0·3282 (5)	2·5
C(1)	0·2784 (27)	−0·1516 (30)	0·4199 (7)	3·5
C(2)	0·1775 (27)	−0·1471 (24)	0·3399 (5)	2·5
C(3)	0·2875 (26)	−0·0149 (24)	0·3237 (5)	1·8
C(4)	0·3306 (30)	−0·0448 (26)	0·2804 (6)	2·7
C(5)	0·5166 (39)	−0·1945 (49)	0·2396 (7)	3·1

Table 3. *Bond distances* (Å) *and angles* (°)

Pd–Cl(1)	2·319 (5)	C(2)–C(3)	1·53 (3)
Pd–Cl(2)	2·300 (6)	C(3)–N	1·49 (3)
Pd–S	2·256 (5)	C(3)–C(4)	1·53 (3)
Pd–N	1·971 (16)	C(4)–O(1)	1·18 (3)
S–C(1)	1·845 (23)	C(4)–O(2)	1·40 (3)
S–C(2)	1·788 (20)	O(2)–C(5)	1·44 (3)
Cl(1)–Pd–Cl(2)	94·4 (2)	C(1)–S–C(2)	102·6 (10)
Cl(1)–Pd–S	175·4 (2)	S–C(2)–C(3)	109·8 (14)
Cl(1)–Pd–N	89·0 (5)	N–C(3)–C(2)	106·8 (16)
Cl(2)–Pd–S	90·2 (2)	N–C(3)–C(4)	110·7 (16)
Cl(2)–Pd–N	176·2 (5)	C(2)–C(3)–C(4)	111·5 (17)
S–Pd–N	86·4 (5)	C(3)–C(4)–O(1)	127·6 (21)
Pd–S–Cl	104·0 (8)	C(3)–C(4)–O(2)	109·0 (18)
Pd–S–C(2)	99·0 (7)	O(1)–C(4)–O(2)	123·4 (21)
Pd–N–C(3)	111·9 (12)	C(4)–O(2)–C(5)	116·2 (20)

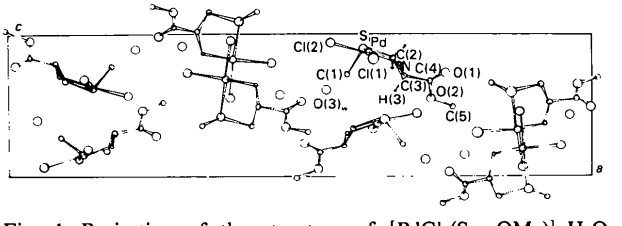

Fig. 1. Projection of the structure of $[PdCl_2(SmcOMe)].H_2O$ along **b**.

Description and discussion of the structure

The crystal structure consists of monomeric $[PdCl_2(SmcOMe)]$ units which are hydrogen bonded through the water of crystallization.

The bidentate *S*-methyl-L-cysteine methyl ester ligand coordinates to the Pd through the S and N donors forming a five-membered chelate ring. Two Cl atoms are bonded to the Pd in *cis* positions as required by the geometry of the chelating SmcOMe ligand. The coordination around Pd is slightly distorted square planar. The deviation of the Pd atom from the

least-squares plane through the four donors is 0·020 (2) Å (Table 4). The Cl(1)—Pd—Cl(2) angle, 94·4 (2)°, is greater than N—Pd—S, 86·4 (5)°, which is also the case for the corresponding complex [$PdCl_2$(*S*-methyl-L-cysteine)] [95·5 (2) and 87·2 (3)°] (Battaglia *et al.*, 1973) and for [$PdCl_2$(*S*-methyl-L-cysteine sulfoxide)] [94·0 (2) and 86·8 (5)°] (Allain *et al.*, 1980). The Pd—Cl, Pd—S and Pd—N distances are comparable with the values found in related complexes.

Table 4. *Least-squares planes*

Deviations (Å) of relevant atoms from the planes are given with their e.s.d.'s in parentheses.

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

$$-0{\cdot}9574X + 0{\cdot}0676Y - 0{\cdot}2807Z + 4{\cdot}6016 = 0$$

Cl(1) 0·002 (6), Cl(2) −0·002 (6), S 0·002 (5), N −0·022 (16), Pd 0·020 (2)

Plane (2) through Pd, S, N

$$-0{\cdot}9522X + 0{\cdot}0578Y - 0{\cdot}3000Z + 4{\cdot}8411 = 0$$

Cl(1) −0·032 (6), Cl(2) −0·070 (6), O(1) 0·115 (18), O(2) −1·678 (18), C(1) −1·700 (22), C(2) −0·087 (22), C(3) −0·730 (21), C(4) −0·644 (24), C(5) −1·77 (3), H(3) −1·71

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

$$-0{\cdot}9592X + 0{\cdot}0768Y - 0{\cdot}2721Z + 4{\cdot}4586 = 0$$

S −0·036 (5), N −0·062 (16)

Plane (4) through Pd, S, N, C(2)

$$-0{\cdot}9475X + 0{\cdot}0545Y - 0{\cdot}3151Z + 5{\cdot}0357 = 0$$

Pd 0·0, S 0·004 (5), N 0·031 (16), C(2) −0·054 (22), C(1) −1·704 (22), C(3) −0·688 (21), C(4) −0·578 (24), O(1) 0·191 (17), O(2) −1·603 (18)

Plane (5) through O(1), O(2), C(3), C(4)

$$-0{\cdot}6728X - 07381Y - 0{\cdot}0503Z + 2{\cdot}0642 = 0$$

O(1) −0·003 (17), O(2) −0·002 (18), C(3) −0·003 (20), C(4) 0·013 (23), C(5) −0·039 (37), N −0·465 (16), C(2) 1·395 (21)

Interplanar angles (°) (e.s.d.'s 1–2°)

(1)–(2)	1·3	(2)–(3)	2·0
(1)–(4)	2·2	(2)–(5)	52·2
(1)–(5)	52·5	(4)–(5)	52·2

The bond lengths and angles in the amino acid are similar to those reported for a variety of metal complexes of *S*-methyl-L-cysteine (Battaglia *et al.*, 1973) and its derivatives (Allain *et al.*, 1980; Nicholls & Freeman, 1979) and agree well with the average values in amino acids (Marsh & Donohue, 1967). The C—O lengths in the carboxyl moiety of the ester group, 1·18 (3) and 1·40 (3) Å, are in agreement with those found in carboxylic esters (Kanters, Kroon, Peederman & Schoone, 1967).

The five-membered chelate ring shows an envelope-like conformation, with C_α(3) deviating −0·69 (2) Å from the plane through N, Pd, S, C(2). C_β(2) and C_α(3) lie −0·09 (2) and −0·73 (2) Å respectively from the S—Pd—N plane. In the corresponding [$PdCl_2$(Smc)] and [$PdCl_2$(SOmc)] complexes, C_α and C_β are situated on opposite sides of the plane of coordination of the chelate ring. The carboxyl group is planar, with the N atom 0·47 Å out of this plane. The conformation of the ligand molecule is described by the torsion angles in Table 5 and the Newman projections in Fig. 2. The values of these angles are in agreement with those calculated for the related metal complexes cited above. As can be seen from Table 5, another special conformational feature of this molecule is the *S*-methyl-L-cysteine methyl ester ring with the carboxyl group in a position which is not clearly axial or equatorial. In comparison with [$PdCl_2$(SOmc)].H_2O, the carboxyl group is twisted by about 30° around the C_α—C bond. A probable reason for this twist of the carboxyl group is an intramolecular interaction of O(1) and O(2) with the NH_2 and $C_\beta H_2$ groups. In comparison with [$PdCl_2$(SOmc)], where the $C_\beta \cdots O$ van der Waals contact is only 2·81 Å, increase in the negative value of ψ_1 in this structure produces a more favorable non-bonded $C_\beta(3) \cdots O(2)$ contact (3·12 Å). As noted by Sundaralingam & Putkey (1970), the preferred value of ψ_1 is centered at about −15° for the amino acid.

The ester group has the antiplanar conformation [torsion angle C(5)—O(2)—C(4)—C(3) = −177·8 (25)°] typical of esters, with C(5)···O(1) and

Table 5. *Conformations of chelate rings in* Pd^{II} *complexes with S-methyl-L-cysteine and its derivatives*

	ψ_1	ψ_2	χ	φ	Pd—S—N ∧ C—O—O	Reference
$PdCl_2$[(3*R*,S*R*)-*S*-methyl-L-cysteine methyl ester]	−17·7 (30)°	160·0 (23)°	−51·0 (17)°	−81·7 (25)°	52·2°	(*a*)
$PdCl_2$[(*R*,*S*)-*S*-methyl-L-cysteine sulfoxide]	11·1	−171·6	−48·5	156·7	12·1	(*b*)
$PdCl_2$[(*R*,*R*)-*S*-methyl-L-cysteine]*	7·5	−174·4	−52·5	−78·9	11·3	(*c*)
$PdCl_2$[(*R*,*S*)-*S*-methyl-L-cysteine]	10·5	168·7	−60·0	149·6	7·1	(*c*)

Rotation angles are defined according to IUPAC–IUB Commission on Biochemical Nomenclature (1970): $\psi_1 = \tau$[O(1)C(4)C(3)N]; $\psi_2 = \tau$[O(2)C(4)C(3)N]; $\chi = \tau$[NC(3)C(2)S]; $\varphi = \tau$[C(1)SC(2)C(3)].

References: (*a*) this work; (*b*) Allain *et al.* (1980); (*c*) Battaglia *et al.* (1973).

* Includes two crystallographically independent molecules.

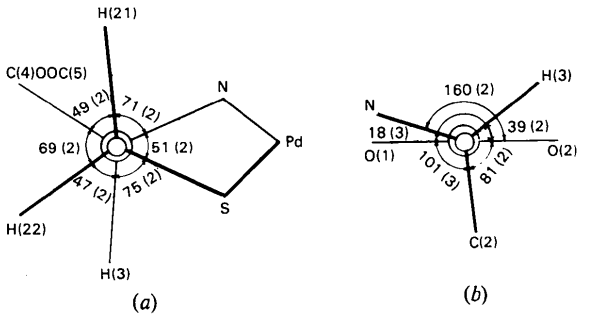

Fig. 2. Newman projections along (*a*) C(2)–C(3) and (*b*) C(3)–C(4).

C(5)···C(4) distances of 2·71 (4) and 2·42 (4) Å, respectively.

The *S*-methyl-L-cysteine methyl ester ligand has a single asymmetric center at C_α, but the coordination introduces a chiral center at the S atom. In [$PdCl_2$(*S*-methyl-L-cysteine methyl ester)] both asymmetric centers have the same *R*,*R* configurations. Both chiralities are found in the crystal structure of [$PdCl_2$(*S*-methyl-L-cysteine)] (Battaglia *et al.*, 1973); there are two crystallographically independent molecules and their S donor atoms have configurations of opposite handedness. It would be interesting to find if there is any stereospecificity upon coordination in the formation of the chiral center at the S atom.

In the actual structure the methyl group is in a pseudo-axial position relative to the plane of the chelate ring, with torsion angle C_M–S–C_β–C_α = −81·7 (17)°. A comparison of this value with those computed from the data of Battaglia *et al.* (1973) and Allain *et al.* (1980) (Table 5) indicates that a pseudo-axial methyl group is usually connected with an *R* configuration of the S atom.

The arrangement of molecules viewed along (010) is shown in Fig. 1. Packing contacts which can be considered as hydrogen bonds are:

N···Cl(2)^{i}	3·37 (2) Å	N–H(2)N···Cl(2)^{i}	142·4 (9)°
$O(3)_w$···N^{i}	2·91 (3)	$O(3)_w$···H(1)N–N^{i}	157·3 (11),
$O(3)_w$···$O(3)_w^{ii}$	2·84 (3)		

with the symmetry code (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}-z$, (ii) $y, x, 1-z$.

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