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Dichloro[(2*S*,S*R*)-*S*-methylcysteine *S*-oxide]platinum(II) Hydrate

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(*Received* 4 *December* 1978; *accepted* 8 *June* 1979)

Abstract. $[Pt(C_4H_9NO_3S)Cl_2].H_2O$, $M_r = 435{\cdot}30$, monoclinic, $C2$, $a = 17{\cdot}721$ (7), $b = 5{\cdot}386$ (2), $c = 11{\cdot}781$ (4) Å, $\beta = 104{\cdot}8$ (1)° (at 294 K), $V = 1090{\cdot}2$ (11) Å^3, $\mu = 13{\cdot}92$ mm^{-1} (Mo $K\alpha$), $D_o = 2{\cdot}65$ (2), $D_c = 2{\cdot}653$ Mg m^{-3} ($Z = 4$). The amino acid coordinates to Pt^{II} through N and S. The five-membered chelate ring has the λ conformation and an equatorial carboxyl group. The S—O and S—CH_3 bond vectors make almost equal angles with the plane of coordination (50·1 and 57·8° respectively). The Pt—S distance of 2·182 (3) Å is the shortest Pt—S distance found thus far in any Pt^{II} complex.

Introduction. The title compound was prepared by combining stoichiometric amounts of K_2PtCl_4 and (2*S*,S*R*)-*S*-methylcysteine *S*-oxide in hot aqueous solution, in an adaptation of the method used by Volshtein & Mogilevkina (1963) to make $PtCl_2$-(methionine). It was recrystallized from hot dilute HCl. The prismatic crystal used in this work had the dimensions 0·38 × 0·079 × 0·061 mm.

The space group $C2$ was unambiguously determined from the systematic absences, $h + k$ odd for all hkl, noted on precession photographs; the compound was known to be optically active. The crystal was mounted on a Picker FACS-1 computer-controlled four-circle diffractometer. Accurate cell dimensions were obtained by a least-squares refinement of the setting angles of 12 general reflections having 2θ in the range 45–50° and using Mo $K\alpha_1$ radiation. The crystal was accurately aligned with [010] coincident with the φ axis of the diffractometer. To determine the severity of the absorption problem the 020 reflection was measured (by repeated θ–2θ scans) at $\chi = 90°$ and at 10° intervals from $\varphi = 0°$ to $\varphi = 350°$. The variation in intensity as a function of φ (defined as maximum − minimum/average) was 20%. The data were corrected for absorption. Data-collection procedures and computer programs for the reduction of the data, for the application of an empirical correction to account for absorption by the β filter, for the absorption correction, and for solution and refinement of the structure were as described by Churchill & DeBoer (1973). Details specific to this case are summarized in Table 1.

A set of 1928 unique data was collected out to a 2θ of 50°. During the latter stages of refinement it was found that a small subset of these was systematically low. Review of the data-collection procedures and the standards gave evidence for intermittent instrument malfunction. Ultimately seven (hkl, $h\bar{k}l$) pairs for which $\Delta F_{obs}/\sigma > 20$ were omitted from the analysis.

An original 'observed' Fourier synthesis phased by the Pt alone allowed location of all the donor atoms; all non-hydrogen light atoms were then found in successive difference Fourier analyses. Calculations were performed on an IBM 370/158 computer. Atom scattering factors were taken from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). Refinement included the use of anisotropic thermal parameters for all non-hydrogen atoms and insertion of nine 'riding' H atoms (all the non-water H atoms) in idealized positions with d(N—H) = 0·87 Å, d(C—H) = 0·95 Å (Churchill, 1970). The positional parameters of the H atoms were constrained to vary with the positional parameters of their attached C or N atoms. An overall isotropic thermal parameter for all the H

* To partially fulfill requirements for a PhD at UICC (1977).

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Table 1. *Experimental data*

(*a*) Measurement of intensity data

Radiation: Mo $K\alpha$. Filter: Nb foil at counter aperture (~47% transmission of Mo $K\alpha$). Attenuator: Cu (inserted when $I > 10^4$ counts s^{-1}).

Take-off angle: 3·0°. Detector aperture: 6·4 × 6·4 mm. Crystal–detector distance: 300 mm. Crystal orientation: mounted on [010].

Reflections measured: $h, \pm k, \pm l$.

Scan type: coupled θ(crystal)–2θ(counter). Scan speed: 2·0° min^{-1}. Scan length: $\Delta(2\theta) = (1{\cdot}2 + 0{\cdot}692 \tan\theta)°$, starting 0·6° below the Mo $K\alpha_1$ peak.

Background measurement: stationary crystal, stationary counter, 20 s each at beginning and end of 2θ scan.

Standard reflections: three measured after every 48 reflections; r.m.s. deviations (after application of anisotropic linear decay correction)* were 3·25% for 002, 1·23% for 020 and 3·33% for $\bar{2}05$.

Maximum 2θ: 50°

Reflections collected: 1928 measurements and no systematic absences.

(*b*) Treatment of intensity data

Conversion to $|F_o|$ and $(\sigma|F_o|)$: as in Churchill & DeBoer (1973), using an 'ignorance factor' of $p = 0{\cdot}04$.

Absorption coefficient: $\mu = 13{\cdot}92$ mm^{-1}; maximum and minimum transmission factors were 49·1 and 36·1% respectively.†

(*c*) Details of refinement

Unique data used: 1914.

Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$, by full-matrix least squares.

Final number of variables: 117 independent, 36 dependent (for 'riding' hydrogen atoms).

Final error in observation of unit weight: 1·88.

Final $R_F = 0{\cdot}0336$ $R_{Fw} = 0{\cdot}0520$.

* Data reduction (including averaging, linear-decay correction, *etc.*) was performed using the Fortran IV program *RDUS* by B. G. DeBoer.

† Absorption corrections were carried out using the Fortran IV program *DRABZ* by B. G. DeBoer.

atoms bonded to each C or N was held equal to 1·1 times the isotropic parameter of the attached C or N.

Both the real and imaginary components of anomalous dispersion were used for all non-hydrogen atoms (Cromer & Liberman, 1970). The final discrepancy indices for the solution were $R_F = 0{\cdot}0336$ and $R_{wF} = 0{\cdot}0520$. The 'goodness-of-fit' was 1·88. During the final stages of refinement the handedness of the model was reversed (Hamilton, 1965) to give discrepancy indices of $R_F = 0{\cdot}0554$ and $R_{wF} = 0{\cdot}0793$. This result verified the correctness of the enantiomorphism of the model. The grestest Δ/σ for any parameter in the last cycle of refinement was 0·005. The final positional parameters are given in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34530 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final positional parameters for the atoms in the title compound*

Estimated standard deviations, shown in parentheses, are right-adjusted to the last digit of the preceding number and were derived from the inverse of the final least-squares matrix.

	x	*y*	*z*
Pt	0·38645 (2)	$\frac{1}{4}$	0·24623 (3)
Cl(1)	0·4351 (3)	0·1945 (11)	0·0848 (3)
Cl(2)	0·4592 (2)	−0·0785 (7)	0·3383 (3)
S	0·3307 (2)	0·3128 (5)	0·3896 (3)
O(1)	0·2299 (6)	0·9513 (20)	0·0935 (9)
O(2)	0·1452 (6)	0·8432 (20)	0·2018 (9)
O(3)	0·2830 (6)	0·1071 (18)	0·4211 (9)
O(4)	0·0703 (9)	1·2575 (41)	0·1369 (15)
N	0·3203 (6)	0·5389 (22)	0·1634 (9)
C(1)	0·2069 (8)	0·8093 (23)	0·1592 (11)
C(2)	0·2513 (9)	0·5792 (27)	0·2070 (13)
C(3)	0·2698 (9)	0·5731 (25)	0·3385 (12)
C(4)	0·3933 (10)	0·4260 (33)	0·5176 (12)
H(C2)	0·2186 (9)	0·4438 (27)	0·1754 (13)
H(C41)	0·3649 (10)	0·4493 (33)	0·5755 (12)
H(C42)	0·4151 (10)	0·5800 (33)	0·5024 (12)
H(C43)	0·4338 (10)	0·3091 (33)	0·5448 (12)
H(O2)	0·0930 (6)	0·8647 (20)	0·1387 (9)
H(C31)	0·2230 (9)	0·5590 (25)	0·3637 (12)
H(C32)	0·2959 (9)	0·7223 (25)	0·3685 (12)
H(N1)	0·3073 (6)	0·5093 (22)	0·0885 (9)
H(N2)	0·3484 (6)	0·6728 (22)	0·1769 (9)

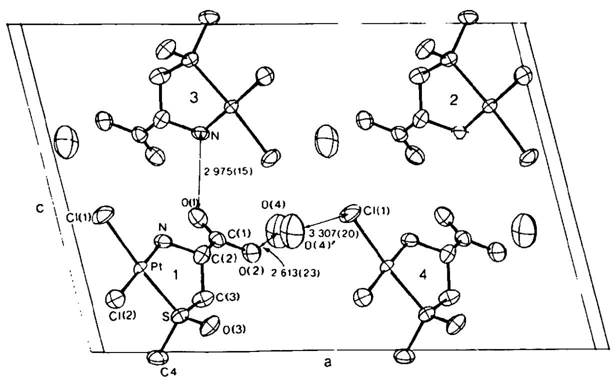

Fig. 1. General perspective view of a unit cell of $Pt(C_4H_9NO_3S)Cl_2.H_2O$ ($Z = 4$) approximately down the *b* axis. An additional molecule of water [O(4)′], a member of the neighboring unit cell immediately above the cell sketched, is included to indicate important non-bonding interactions. Molecules 1 and 2, and 3 and 4 are related by the twofold axis; 1 and 3, and 2 and 4 are related by the twofold screw axis. Some close non-bonded approaches are shown. Distances are in Å, H atoms are omitted.

Discussion. The title compound was prepared as part of a study of the effects of *S*-oxidation upon the coordination, conformation, and spectra of complexes of sulfur-containing amino acids with Pt^{II}. Beyond this is the continued interest in *cis*-dichloro(ligand)-platinum(II) complexes as antitumor and antiviral agents (Cleare & Hoeschele, 1973).

The structure consists of discrete, approximately square-planar molecules. The Pt atom and its four donors are nearly coplanar. The deviations from the least-squares plane are: Pt 0·0282 (3), Cl(1) 0·025 (5), Cl(2) 0·010 (4), S 0·026 (3), and N 0·013 (11) Å. These molecules are hydrogen-bonded through O(2) to the water of crystallization, O(4). An intermolecular hydrogen bond occurs from N to O(1) in the 2_1-related molecule (see Fig. 1). Other intermolecular approaches include O(1) to the Pt of the molecule related by translation along the b axis [3·328 (10) Å] and N to Cl(2) in the same translationally related molecule [3·474 (12) Å]. (2S,SR)-S-Methylcysteine S-oxide acts as a bidentate ligand; it forms a *gauche* five-membered chelate ring in the λ conformation by coordinating through N and S donors. The carboxylic acid group is uncoordinated (Fig. 2).

Pt^{II} shows a considerable and general preference for S over O donors in ambidentate ligands. For example, both $PtCl_2$[(2S)-S-methylcysteine] and $PtCl_2$[(2S)-cysteine] involve coordination only at the N and S donors (Livingstone & Nolan, 1968). Use of the S-oxide of S-methylcysteine does not change this preference.

However, the presence of the O atom does cause an interesting shortening of the Pt—S bond in this molecule, relative to its length in comparison structures. It is the shortest Pt—S bond yet reported. At 2·182 (3) Å, it is significantly shorter than the 2·278 (7) Å found in *cis*-$PtCl_2[S-(p\text{-}C_6H_4Cl)]_2$ (Spofford, Amma & Senoff, 1971) or the 2·239 (3) Å in $PtCl_2[F_3C-S-CH(CH_3)CH_2SCF_3]$ (Manojlović-Muir, Muir & Solomon, 1977), a case that is more comparable because in it the donor S also bears an electron-withdrawing substituent. The Pt—S bond is also shorter than the 2·26 Å found in $PtCl_2$[(RS)-methionine] (Freeman & Goulomb, 1970), or the 2·265 Å in $PdCl_2$[(RS)-methionine] (Warren, McConnell & Stephenson, 1970); it is shorter than the Pd—S length of 2·230 (4) Å found in $PdCl_2$[(2S)-S-methylcysteine] (Battaglia, Corradi, Palmieri, Nardelli & Tani, 1973). This last is a chelate with a similar ring conformation (see below). The Pt—S length is closest to the Pt—S length of 2·198 (2) Å in $PtCl_2$[(2S,SR)-methionine S-oxide] (Freeman, 1977).

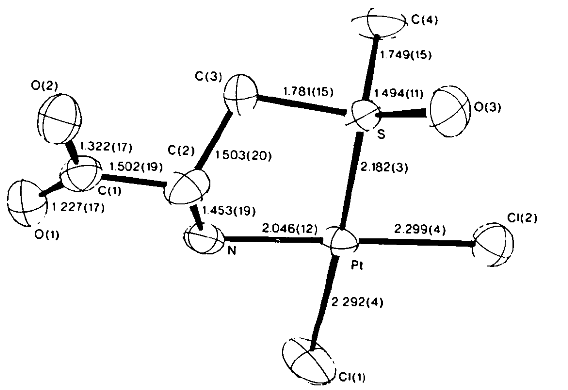

Fig. 2. Perspective view of a molecule of $Pt(C_4H_9NO_3S)Cl_2$. This view is roughly perpendicular to the plane of coordination. The carboxyl group is equatorial. H atoms are omitted for clarity. Interatomic distances are in Å. E.s.d.'s are shown in parentheses and are right-adjusted to the last digit of the preceding number. Their calculation includes the effects of all elements of the positional covariance matrix as well as the uncertainties in unit-cell dimensions. No corrections have been applied for the effects of thermal motion. Ellipsoids are drawn to include 50% probability.

It has been well established that the presence of electron-withdrawing substituents on a donor tends to shorten and presumably to strengthen the metal—donor bond. Much work has been done with P compounds (Pidcock, Richards & Venanzi, 1962) but there is relatively little data on S compounds. The Pt—S bond distances just given, however, do show a similar trend. An additional instance is the bridged thioether complex, $\mu\text{-}[S(C_2H_5)_2]_2\text{-}(PtBr_2)_2$ (Sales, Stokes & Woodward, 1968) where d(Pt—S) is 2·25 (1) Å. In this case both pairs of electrons of the thioethers are involved as donors to Pt leaving the S donor deficient in electron density.

A simple electronic theory explains the extra shortening of the Pt—S(oxide) bond relative to the comparison cases where the donor S also bears electron-withdrawing substituents: donation of $d\pi$ Pt electron density to the empty π^* molecular orbitals of the S—O moiety.

Although similar extra shortening of the Pt—S(oxide) bond is present in $PtCl_2$[(2S,SR)-methionine S-oxide], that complex (Freeman, 1977) also exhibits a structural *trans* effect in the Pt—Cl distances. Such an effect was not found in $PtCl_2$[(2S,SR)-S-methylcysteine S-oxide] (see Fig. 2). These bond distances as well as the other distances and angles (Fig. 2 and Table 3) are within normal ranges found in comparable compounds.

The conformation of the chelate ring in $PtCl_2$-[(2S,SR)-S-methylcysteine S-oxide] is worth comparing to conformations found in similar complexes.

Table 3. *Bond angles (°) with e.s.d.'s for the title compound*

See Fig. 2 for numbering of atoms and explanations of e.s.d.'s.

Cl(1)—Pt—Cl(2)	90·58 (16)	O(3)—S—C(4)	108·8 (7)
Cl(1)—Pt—N	89·5 (3)	C(3)—S—C(4)	102·7 (7)
Cl(2)—Pt—S	93·54 (13)	Pt—N—C(2)	112·2 (9)
S—Pt—N	86·3 (3)	N—C(2)—C(3)	111·7 (12)
Cl(1)—Pt—S	175·02 (14)	N—C(2)—C(1)	113·6 (12)
Cl(2)—Pt—N	179·1 (5)	C(1)—C(2)—C(3)	111·5 (12)
Pt—S—O(3)	117·9 (4)	S—C(3)—C(2)	109·1 (10)
Pt—S—C(3)	102·2 (5)	C(2)—C(1)—O(1)	121·7 (12)
Pt—S—C(4)	114·2 (5)	C(2)—C(1)—O(2)	112·2 (11)
O(3)—S—C(3)	109·6 (7)	O(1)—C(1)—O(2)	125·9 (12)

Table 4. *Conformations of chelate rings in* $PdCl_2$[(2*S*)-*S-methylcysteine*].H_2O *and* $PtCl_2$[(2*S*,*SR*)-*S-methylcysteine S-oxide*].H_2O

Dihedral angles	$PdCl_2$[(2*S*)-*S*-methylcysteine]. H_2O	$PtCl_2$[(2*S*,*SR*)-*S*-methylcysteine *S*-oxide]. H_2O
O(2)–C(1)–C(2) ∧ C(1)–C(2)–N	168·7° (174·4°)*	179·0°
O(1)–C(1)–C(2) ∧ C(1)–C(2)–N	7·5 (10·5)	2·7
N–C(2)–C(3) ∧ C(2)–C(3)–S	52·5 (60·0)	45·9
M–N–S ∧ C(1)–O(1)–O(2)	11·3 (7·1)	27·9

* Includes two crystallographically independent molecules.

The ring is basically similar in its conformation to that found in $PdCl_2$[(2*S*)-*S*-methylcysteine] (Battaglia *et al.*, 1973). {The structure of $PtCl_2$[(2*S*)-*S*-methylcysteine] is unfortunately not available for comparison, so Table 4 presents a comparison of ring dihedral angles to those in the Pd complex.} The presence of the *S*-oxide on the ring corresponds to a decrease in the angle which the S–CH_3 bond makes with the plane of coordination; the angle of the carboxyl group to the same plane is meanwhile greater than in the Pd(*S*-methylcysteine) comparison complex. It had been observed (Freeman, 1977) that the use of the (2*S*,*SR*)-methionine *S*-oxide ligand in place of the unoxidized (2*S*)-methionine resulted in a radical change in the conformation of the six-membered chelate ring formed by that homologous ligand. The complex $PtCl_2$[(2*S*,*SR*)-methionine *S*-oxide] has the –COOH side group axial although this group is always equatorial in studies of chelation of non-*S*-oxidized methionine. A parallel effect was not observed here. The five-membered chelate ring in $PtCl_2$[(2*S*,*SR*)-*S*-methylcysteine *S*-oxide] remains similar in conformation, as seen above, to that in the Pd complex of the non-*S*-oxidized ligand.

Conventional conformational analysis shows that the (2*S*,*SR*)-ligand stereochemistry requires in the λ conformation that an equatorial –COOH group go with an equatorial S–CH_3 and an axial S–O. In the actual structure, the bond vector S–CH_3 makes an angle of 57·8° with the Pt–N–S plane and the bond vector S–O an angle of 51·0°. Neither is clearly axial or equatorial. The C–COOH vector subtends an angle of 27·8° to the plane of coordination (Pt–N–S). Table 4 compares other values to those computed from the data of Battaglia *et al.* (1973).

We would like to thank B. G. DeBoer and C. F. Liu for technical assistance and advice. The generous provision of computer time by the University of Illinois at Chicago Circle Computer Center is gratefully acknowledged.

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