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Dichloro(D-methionine-*N*,*S*)-platinum(II) at 130 K

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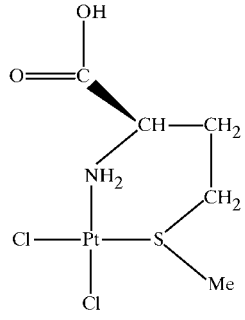
The asymmetric unit of the title compound, $[PtCl_2(C_5H_{11}NO_2S)]$, a D-methionine derivative, contains two molecules with opposite chirality at the S atoms. The amino acid acts as a bidentate ligand and coordinates simultaneously through the N (amino) and S (thioether) atoms. The molecules are packed in pairs which are connected through two hydrogen bonds between the protonated carboxyl groups, with O···O distances of 2.633 (10) and 2.663 (12) Å.

Comment

The use of transition metal complexes, in particular those of platinum group metals, in cancer chemotherapy has been widely reported (Rosenberg *et al.*, 1965; Sherman & Lippard, 1987; Lippert, 1989). Methionine inhibits nephrotoxicity of the *cis*-diamminedichloroplatinum(II) complex (Burchenal *et al.*, 1978), which is in turn widely used clinically as an antiviral and antitumor agent against a range of human cancers (Farrell, 1989). Consequently, there is great interest in the study of the interaction between methionine and platinum(II). To date, the X-ray structures of the $[PtCl_2$(DL-Met)] and $[PtCl_2$(L-Met)] complexes, where DL-Met and L-Met are DL- and L-methionine, have been described (Wilson *et al.*, 1992; Freeman & Golomb, 1970). Wilson and co-workers (1992) have redetermined the structure of $[PtCl_2$(L-Met)] reported by Freeman & Golomb (1970) using high-resolution data. However, the crystals used by Wilson *et al.* (1992) belonged to the monoclinic space group $P2_1$ and those used in the original structure analysis by Freeman & Golomb (1970) belonged to the triclinic space group $P1$. In this paper, we report and compare with the complexes described above the X-ray structure of $[PtCl_2$(D-Met)], (I), which has been determined at two different temperatures, *i.e.* 294 and 130 K.

The lattice constants of (I) at 294 K are a = 7.339 (1), b = 8.384 (1), c = 8.903 (2) Å, α = 74.52 (2), β = 86.38 (1) and γ = 78.25 (1)°, and the corresponding lattice constants at 130 K are given in the *Experimental* section of this paper. Crystal data at both temperatures are consistent and indicate that the crystals studied in the present work belong to the triclinic space group $P1$. Coordination of methionine to platinum creates a new chiral centre at the S atom, which gives rise to two diastereoisomers, *i.e.* *S* and *R*. The asymmetric unit comprises two independent molecules which correspond to the two diastereoisomers mentioned above, that is, with the same chirality at the C2*A* and C2*B* C atoms, but with the S5*A* and S5*B* S atoms having opposite chiralities. This is a clear case where checking programs give an alert for a possible missed centre of symmetry; however, the difference between both molecules in the asymmetric unit is clear when examining



(I)

the C2*A* and C2*B* atoms. The anomalous scattering contribution also indicates the D-enantiomer, as is shown by the absolute structure parameter −0.006 (12) (Flack, 1983), confirming the chirality of the crystal. Perspective views of the two independent molecules, including the atom labelling, are presented in Figs. 1(*a*) and (*b*). The bond distances and angles with their s.u.'s are given in Table 1. The cell parameters of the triclinic dichloro(L-methionine-*N*,*S*)platinum(II) complex obtained at room temperature (Freeman & Golomb, 1970), a = 7.31 (1), b = 8.91 (1), c = 8.39 (1) Å, α = 74.47 (3), β = 78.13 (3) and γ = 86.40 (3)°, correspond well with (I), indicating that the structures are similar except for a chiral inversion at the C atom linked to the carboxyl group. Wilson and co-workers (1992) have presented a monoclinic dichloro(L-methionine-*N*,*S*)platinum(II) complex also exhibiting two diastereoisomeric molecules with their S atoms having opposite chiralities. In the structure of the racemic crystal (monoclinic space group $P2_1/c$; Freeman & Golomb, 1970), dichloro(DL-methionine-*N*,*S*)platinum(II), the S atoms in the centrosymmetrically related independent molecules of the asymmetric unit obviously have opposite chiralities.

In (I), the Pt atom is coordinated by the methionine N (amino) and S (thioether) atoms, and by two chlorines. Models based on this structure show that considerable strain would be involved in the tridentate coordination of methionine through the amino, thioether and carboxyl groups. Coordination of methionine to platinum(II) through the N and S atoms in dichloro(D-methionine-*N*,*S*)platinum(II) was predicted on the basis of IR, ^{1}H and ^{13}C NMR spectra (Caubet *et al.*, 1992). The geometry around platinum is only slightly distorted from a square-planar coordination. The deviations from the plane defined by N, S and Cl atoms are: for molecule *A*, N2*A* 0.006 (4), S5*A* −0.006 (4), Cl1*A* 0.006 (4), Cl2*A* −0.006 (4),

Pt1*A* −0.023 (3) Å; for molecule *B*, N2*B* 0.033 (4), S5*B* −0.030 (4), Cl1*B* 0.029 (4), Cl2*B* −0.032 (4), Pt1*B* −0.004 (4) Å. The amino acid ligand acts in a bidentate manner and together with the Pt atom forms a six-membered ring. The resulting platinum–methionine chelate ring adopts a half-chair conformation with the carboxyl group equatorial to the ring. The N2/C2/C4/S5 and C2/C3/C4 planes form an angle of 63.5 (6)° in molecule *A* and the equivalent planes in molecule *B* form an angle of 60.6 (8)°. The Pt—S bond lengths in the two independent molecules of the asymmetric unit, 2.234 (4) and 2.274 (4) Å, are not equivalent but are not significantly different from the values of 2.246 (2) and 2.247 (2) Å in dichloro(L-methionine-*N*,*S*)platinum(II) (Wilson *et al.*, 1992). In both diastereoisomers, the Pt—Cl bond distances *trans* to the S atoms, 2.329 (3) and 2.310 (3) Å, are similar to the Pt—Cl bond distances *trans* to the N atoms, 2.312 (3) and 2.317 (3) Å, respectively. In contrast to dichloro(L-methionine-*N*,*S*)platinum(II) (Wilson *et al.*, 1992) and dichloro(*O*-methyl-L-methionine-*N*,*S*)platinum(II) (Hambley & Webster, 1994), where the Pt—Cl bond distances *trans* to S [2.323 (2), 2.320 (2) and 2.314 (2) Å] are marginally longer than those *trans* to N [2.309 (2), 2.310 (3) and 2.288 (2) Å, respectively], there is no structural *trans* effect in (I).

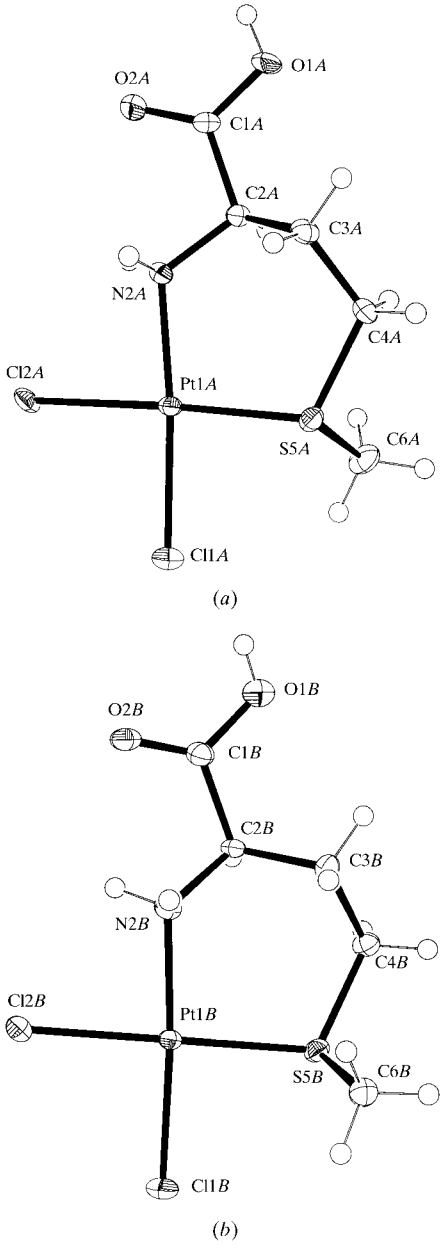


Figure 1
The molecular structure of the two independent molecules of (I), *i.e.* (*a*) molecule *A* and (*b*) molecule *B*, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

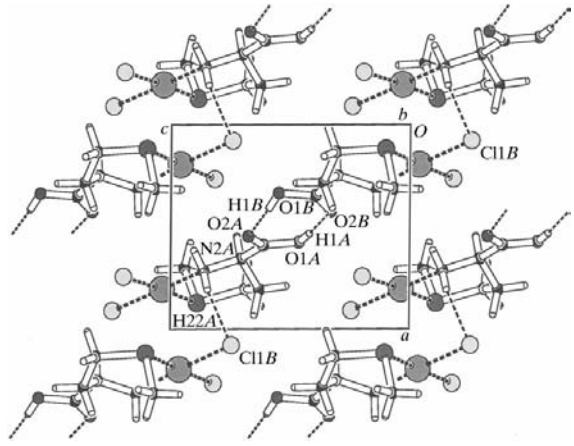


Figure 2
Drawing of the unit cell of (I) along the *b* axis. Dashed lines indicate hydrogen bonds.

The distances N2*A*···O2*A* and N2*B*···O2*B* of 2.662 (14) and 2.600 (13) Å, respectively, suggest the presence of intramolecular hydrogen bonds. On the other hand, intermolecular distances show all acidic H atoms to be involved in hydrogen bonding. The crystal packing is depicted in Fig. 2. Different diastereoisomers form dimers by means of strong hydrogen bonds between their carboxyl groups. The lengths of the O···O hydrogen-bonding distances are 2.663 (12) and 2.633 (10) Å. The shortest Pt···Pt distance is 3.5642 (6) Å. Similar pairing arrangements of molecules due to strong hydrogen bonding are common in molecules containing carboxyl groups. In (I), the D chirality at C atoms bonded to carboxyl groups together with opposite chirality at the S atoms of the two diastereoisomers prevents the formation of a geometry centre between the carboxyl groups.

Experimental

Dichloro(D-methionine-*N*,*S*)platinum(II) was prepared by the interaction of $[PtCl_4]^{2-}$ with methionine in aqueous solution.

Crystal data

$[PtCl_2(C_5H_{11}NO_2S)]$
M_r = 415.2
Triclinic, *P*1
a = 7.265 (1) Å
b = 8.361 (1) Å
c = 8.885 (1) Å
α = 74.95 (1)°
β = 86.04 (1)°
γ = 77.87 (1)°
V = 509.49 (11) Å^3
Z = 2
D_x = 2.706 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 10–29°
μ = 14.46 mm^{-1}
T = 130 (2) K
Prismatic, yellow
0.62 × 0.46 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical *MolEN* (Fair, 1990)
T_{min} = 0.038, T_{max} = 0.074
6153 measured reflections
6153 independent reflections
5719 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 30.4°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F)$ = 0.038
$wR(F^2)$ = 0.097
S = 1.03
6153 reflections
223 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2 + 1.2102P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 1.97 e Å^{-3}
$\Delta\rho_{min}$ = −2.46 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0037 (6)
Absolute structure: Flack (1983)
Flack parameter: −0.006 (12)

Table 1
Selected geometric parameters (Å, °).

Pt1*A*—Cl1*A*	2.312 (3)	Pt1*B*—Cl1*B*	2.317 (3)
Pt1*A*—Cl2*A*	2.329 (3)	Pt1*B*—Cl2*B*	2.310 (3)
Pt1*A*—S5*A*	2.234 (4)	Pt1*B*—S5*B*	2.274 (4)
Pt1*A*—N2*A*	2.044 (10)	Pt1*B*—N2*B*	2.045 (10)
C1*A*—O1*A*	1.302 (12)	O2*B*—C1*B*	1.202 (14)
C1*A*—O2*A*	1.214 (13)	O1*B*—C1*B*	1.318 (13)
Cl2*A*—Pt1*A*—N2*A*—C2*A*	−162.7 (8)	Cl2*B*—Pt1*B*—N2*B*—C2*B*	−149.0 (9)
Pt1*A*—N2*A*—C2*A*—C3*A*	−54.5 (10)	Pt1*B*—N2*B*—C2*B*—C3*B*	−62.9 (11)
C1*A*—C2*A*—C3*A*—C4*A*	−153.4 (8)	C1*B*—C2*B*—C3*B*—C4*B*	−159.8 (8)

H atoms were treated as riding on the C atoms (C—H = 0.96–0.98 Å) to which they are attached and refined with a global isotropic displacement parameter.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 1998); software used to prepare material for publication: *WINGX* (Farrugia, 1999).

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*^{i}	0.82	1.82	2.633 (10)	175
O1*B*—H1*B*···O2*A*^{ii}	0.82	1.86	2.663 (12)	166
N2*A*—H22*A*···Cl1*B*^{iii}	0.90	2.52	3.401 (10)	168

Symmetry codes: (i) $x, 2+y, z$; (ii) $x, y-2, z$; (iii) $1+x, 1+y, 1+z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1045). Services for accessing these data are described at the back of the journal.

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