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Dichloro[(2*S*,S*R*)-methionine sulfoxide]platinum(II) Hydrate

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Abstract. $Pt(C_5H_{11}NSO_3)Cl_2.H_2O$, $M_r = 449{\cdot}22$ orthorhombic, $P2_12_12_1$; $a = 13{\cdot}420\,(4)$, $b = 10{\cdot}888\,(2)$, $c = 8{\cdot}066\,(1)$ Å (at 21 °C), $V = 1178{\cdot}58$ Å^3, $F(000) = 840$, $D_o = 2{\cdot}533\,(5)$, $D_c\ (Z = 4) = 2{\cdot}531$ g cm^{-3}. Crystals were prepared by the direct reaction of the ligand with aqueous K_2PtCl_4, followed by recrystallization from dilute HCl. The Pt atom coordinates through the N and S atoms. The *S*,*R* absolute configuration of the ligand is confirmed by anomalous dispersion. The six-membered chelate ring is in the chair conformation. The carboxylic acid group is axial; the S—CH_3 and S—oxide substituents are equatorial and axial respectively. The complex is distorted from planar coordination and there is a structural *trans* effect.

Introduction. Preliminary precession photographs showed orthorhombic symmetry and the systematic absences: *h*00 for *h* odd, 0*k*0 for *k* odd, 00*l* for *l* odd. The orthorhombic space group $P2_12_12_1$ was thus indicated. A prismatic crystal of approximate dimensions 0·10 × 0·11 × 0·21 mm was used for intensity data collection. It was mounted on a Picker FACS-1 computer-controlled four-circle diffractometer. The crystal was accurately centered and aligned with [002] coincident with the φ axis of the diffractometer.

To ascertain the severity of the absorption problem the 002 reflection was measured (by repeated θ–2θ scans) at $\chi = 90°$, and at 10° intervals from $\varphi = 0$ to 350°. The variation in intensity as a function of φ [defined as maximum–minimum/average] was 31·8% When these φ-scan data were later corrected (along with the primary data set) for the effects of absorption, the variation in intensity was reduced to 10·2%.

Data-collection procedures and computer programs for the reduction of the data, for the application of the absorption correction, for the application of an empirical correction to take account of absorption by the β filter, and for solution and refinement of the structure, were as described by Churchill & DeBoer (1973). Details pertinent to this structure are summarized in Table 1.

Calculations were performed on an IBM 370/158 computer. The structure was solved by the heavy-atom method. Atomic scattering factors for neutral non-hydrogen atoms 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 the insertion of ten riding hydrogens in idealized positions [based on d(C—H) = 0·95, d(N—H) = 0·87 Å], as suggested by Churchill (1973). These hydrogens had shifts in positional parameters held equal to the shifts of their attached atoms. An overall isotropic thermal parameter was used for all the H atoms attached to each different non-hydrogen atom.

Both the real and imaginary components of anomalous dispersion were included throughout the refinement for all non-hydrogen atoms (with the values of Cromer & Liberman, 1970). During the final stages of refinement a reversal of handedness to the enantio-

Table 1. *Experimental data for the X-ray diffraction study*

(*a*) Measurement of intensity data

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

Takeoff angle: 3·0°. Detector aperture: 5 mm × 5 mm. Crystal-detector distance: 330 mm. Crystal orientation: mounted on [002]

Reflections measured: $h \pm k\ l$ (one quadrant).

Maximum 2θ: 50°. Scan type: coupled θ(crystal)–2θ(counter).

Scan speed: 1·0° min^{-1}. Scan length: $\Delta(2\theta) = (0{\cdot}6 + 0{\cdot}692\ \tan\theta)°$, starting 0·3° below the Mo $K\alpha_1$ peak.

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

Standard reflections: three remeasured after every 48 reflections; r.m.s. deviations (after application of anisotropic linear decay correction) were 1·62% for 400, 0·97% for 040, 0·66% for 002.

Reflections collected: 2516 independent measurements; of these, 402 were duplicate equivalent measurements (averaged into primary data set), 25 were systematic absences.

(*b*) Treatment of intensity data

Conversion to $|F_o|$ and $(w|F_o|)$: as in Churchill & DeBoer (1973), with an 'ignorance factor' $p = 0{\cdot}03$.

Absorption coefficient: $\mu = 132{\cdot}8$ cm^{-1}; maximum and minimum transmission factors were 0·344% and 0·239% respectively.

(*c*) Details of refinement

Unique data used: 2089.

Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$ by full-matrix least squares.

Final number of variables: 132 independent, 35 dependent (for 'riding' H atoms).

Final error in observation of unit weight: 1·282.

Final R_F: 2·96%; R_{WF}: 3·31%.

meric coordinates gave significantly higher discrepancy indices. The absolute configuration of the molecule was thus determined to be that given in Fig. 1 and Table 2. The final conventional R_F (defined as $[\Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|\,] \times 100\%$) was 2·96%*.

Discussion. This compound was prepared and characterized in connection with studies on the effect of chelate ring conformation and vicinal asymmetric centers on circular dichroism of the $\mathrm{Pt^{II}}$ chromophore. Its structure consists of discrete, approximately square-planar molecules of the $\mathrm{Pt^{II}}$ complex hydrogen bonded through the waters of crystallization. Each water of crystallization [oxygen designated O(4)] has one hydrogen bond to each of two molecules of the complex. These molecules are related by the twofold screw axis parallel to the *x* axis. The hydrogen bonds involve atoms O(1) and O(3) of the complex (see Fig. 1 for numbering of atoms). O(3) is the sulfoxide O; O(1) is the protonated carboxylic acid O. [To conclude that O(1) is the protonated O atom, note that in Fig. 1 the distance C(1)–O(1) is significantly greater than C(1)–O(2).] The O(4)–O(1) and O(4)–O(3) distances are 2·579 (11) and 2·804 (10) Å respectively. The angle subtended at O(4) by O(1) and O(3) is 106·0 (4)°. The next shortest intermolecular approach [O(3)–C(3)] is 3·168 (12) Å; all others exceed 3·20 Å.

Interest in this structure lies in the stereochemistry of the platinum–ligand chelate ring. In such a six-membered ring there are two chair conformations and intermediate boat and skew-boat conformations. The absolute configurations at both the chiral centers [C(2)

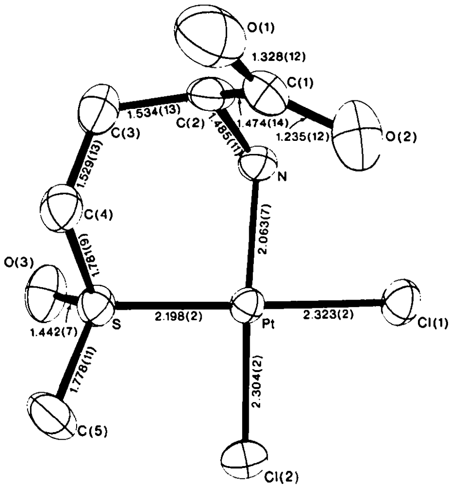

Fig. 1. Perspective view of a molecule of $\mathrm{Pt(C_5H_{11}NSO_3)Cl_2}$ perpendicular to the plane of coordination. The COOH group and O(3) are clearly axial; C(5) (the S—methyl carbon atom) is equatorial to the chelate ring. Hydrogens are omitted. Interatomic distances are in Å. E.s.d.'s are shown 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 for the effects of thermal motion have been applied.

Table 2. *Final parameters for atoms in dichloro* [(2*S*,*SR*)-*methionine sulfoxide*]*platinum*(II) *hydrate*

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. Anisotropic thermal parameters are in units of Å^2 and enter the structure-factor equation in the form $\exp[-0{\cdot}25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0·15896 (2)	0·09300 (3)	0·06832 (4)	2·238 (13)	2·345 (13)	2·049 (12)	−0·146 (12)	0·083 (12)	−0·045 (12)
Cl(1)	0·32403 (17)	0·14406 (23)	0·12091 (30)	2·94 (11)	4·22 (11)	3·30 (11)	−0·88 (9)	−0·30 (8)	0·04 (8)
Cl(2)	0·13669 (18)	0·27258 (23)	−0·07823 (38)	4·11 (11)	3·17 (9)	4·58 (12)	−0·24 (8)	−0·18 (10)	1·46 (10)
S	0·00647 (16)	0·03377 (21)	0·00906 (30)	2·25 (9)	2·48 (9)	3·23 (10)	0·17 (7)	0·17 (8)	−0·05 (8)
O(1)	0·1826 (5)	−0·3333 (6)	−0·0199 (9)	4·6 (4)	3·5 (3)	4·5 (4)	0·4 (3)	−0·0 (3)	−0·2 (3)
O(2)	0·2955 (6)	−0·1811 (7)	0·0014 (10)	3·0 (3)	5·5 (4)	5·4 (4)	−0·1 (3)	−0·2 (3)	−0·7 (3)
O(3)	−0·0703 (5)	0·0730 (7)	0·1225 (9)	2·9 (3)	4·1 (4)	5·3 (4)	0·1 (3)	0·9 (3)	−1·6 (3)
O(4)	0·2748 (6)	−0·4358 (7)	−0·2640 (10)	4·8 (4)	4·1 (4)	5·3 (4)	1·4 (3)	−0·5 (3)	0·1 (3)
N	0·1859 (5)	−0·0549 (6)	0·2218 (10)	2·7 (3)	2·9 (3)	2·6 (3)	−0·4 (2)	−0·4 (3)	0·7 (3)
C(1)	0·2166 (7)	−0·2295 (9)	0·0457 (13)	2·9 (4)	3·6 (4)	3·5 (5)	0·3 (3)	−0·9 (4)	1·1 (4)
C(2)	0·1542 (8)	−0·1822 (7)	0·1818 (12)	3·6 (4)	1·9 (3)	3·5 (4)	0·4 (4)	−0·4 (4)	0·7 (3)
C(3)	0·0413 (7)	−0·1906 (9)	0·1536 (13)	2·9 (4)	3·2 (4)	4·0 (5)	−0·7 (4)	0·2 (4)	−0·3 (4)
C(4)	0·0058 (7)	−0·1294 (8)	−0·0064 (12)	2·7 (4)	2·4 (4)	4·0 (4)	−0·3 (3)	−0·3 (3)	−0·3 (3)
C(5)	−0·0293 (8)	0·0739 (10)	−0·1962 (14)	4·0 (5)	4·1 (6)	4·5 (5)	0·4 (4)	−2·1 (4)	0·8 (5)

	x	y	z	B
NH(1)	0·2490 (5)	−0·0580 (6)	0·2404 (10)	6·9 (25)
NH(2)	0·1548 (5)	−0·0385 (6)	0·3163 (10)	
C(2)H	0·1677 (8)	−0·2369 (7)	0·2731 (12)	1·6 (15)
C(3)H(1)	−0·0096 (7)	−0·1522 (9)	0·2410 (10)	5·4 (20)
C(3)H(2)	0·0241 (7)	−0·2757 (9)	0·1484 (13)	

	x	y	z	B
C(4)H(1)	0·0484 (7)	−0·1540 (8)	−0·0946 (12)	3·9 (17)
C(4)H(2)	−0·0604 (7)	−0·1566 (8)	−0·0295 (12)	
C(5)H(1)	−0·0318 (8)	0·1613 (10)	−0·2028 (14)	6·8 (20)
C(5)H(2)	0·0179 (8)	0·0430 (10)	−0·2711 (14)	
C(5)H(3)	−0·0931 (8)	0·0410 (10)	−0·2173 (14)	

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and S] of the ligand are known to be [*S* and *R*] (Christensen & Kjaer, 1965). These absolute configurations were confirmed in this study. In the complex, since the two centers of asymmetry are of opposite sense, the possible dispositions of the chelate ring substituents corresponding to the two chair conformations are: [—COOH equatorial, S—CH_3 axial, S—oxide equatorial] and [—COOH axial, S—CH_3 equatorial, S—oxide axial]. It is clear in Fig. 1 that the latter conformation was found. The angles of the three substituents to the plane of coordination (plane Pt—N—S) are: —COOH, 84·5; S—CH_3, 36·4; S—oxide, 63·7°. In the X-ray structures of the closely related complexes Pt(*S*-methionine)Cl_2, Pt(*RS*-methionine)Cl_2 (Freeman & Golomb, 1970), and Pd(*RS*-methionine)Cl_2 (Warren, McConnell & Stephenson, 1970) the —COOH equatorial chair conformation was always found. With Pt(*RS*-methionine)Cl_2, the racemic complex, the S—CH_3 group was axial; with Pt(*S*-methionine)Cl_2, the S—CH_3 was axial and equatorial in equal proportion (*i.e.* there was no stereospecificity upon coordination in the formation of the chiral center at the S atom).

The structure of this complex differs in other ways from the related complexes cited above. There is, for example, more distortion from the nominal square-planar geometry. In [Pd(*RS*-methionine)Cl_2], the largest deviation from the least-squares plane through the four donors and the Pd atoms is 0·024 Å; in this complex the deviations are: Pt, 0·011; Cl(1), 0·082; Cl(2), 0·080; N, 0·09 Å. These deviations amount to a twisting of the Pt—N—S plane relative to the Pt—Cl(1)—Cl(2) plane by 6·1 (4)°. The sense of the twisting is to bring the sulfoxide O atom nearer to the Pt atom. The distortion is shown in Fig. 2.

Additionally, the Pt—S bond in this complex is shorter than the analogous bond in the related complexes. It is 2·198 (2) *versus* 2·26, 2·25 and 2·265 (4) Å in [Pt(*RS*-methionine)Cl_2], [Pt(*S*-methionine)Cl_2] and [Pd(*RS*-methionine)Cl_2] respectively.

Finally, there is a distinct *trans* influence on the Pt—Cl bond lengths in this complex that is absent (or nearly absent) in the related thioether S complexes. Here the Pt—Cl distance for the Cl atom *trans* to the S donor is significantly longer [by 0·019 (4) Å] than the Pt—Cl distance for the *cis* Cl atom. In the thioether S complexes, the analogous difference is, for Pd(*RS*-methionine)Cl_2, less than one standard deviation, or, for Pt(*S*-methionine)Cl_2 (for which uncertainties are not quoted), 0·01 Å.

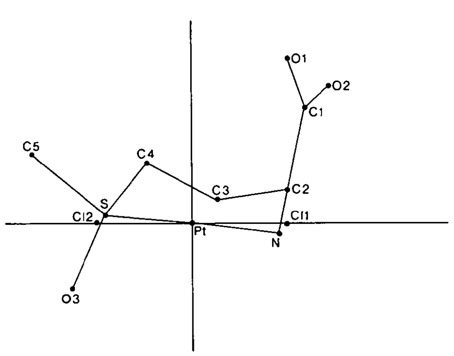

Fig. 2. Projection of a molecule of $Pt(C_5H_{11}NSO_3)Cl_2$ on a plane perpendicular to the Cl(1)—Pt—Cl(2) plane. The plane of coordination of the chelate ring (S—Pt—N) is at an angle of 6·1 (4)° to the plane Cl(1)—Pt—Cl(2).

The obvious sources of the differences between this and the related structures are: different packing and hydrogen bonding (involving a water of hydration not found in the comparison structures) and the extra sulfoxide O atom itself. This latter factor is undoubtedly the predominant cause of the Pt—S shortening, of the appearance of the structural *trans* effect and of the distortion from planar coordination; it is hard to imagine how hydrogen bonds and packing forces alone could effect such changes. In principle either factor could, in this structure, make the chelate ring gain stability with the —COOH axial rather than equatorial. But the Pt—S shortening and the structural *trans* effect indicate that there is added π character in the Pt—S bond when sulfoxide S is coordinated. The [—COOH axial, S—CH_3 equatorial, S—oxide axial] conformation could then be understood qualitatively, in valence-bond terms, as the attainment of a geometry that better allows partial donation of a lone pair of electrons from the metal d_{z^2} orbital to the empty π^* orbital of the S—O moiety.

A molecular-orbital approach, devised to deal with the question of linear *versus* bent transition-metal–nitrosyl complexes (Hoffman, Chen, Elian, Rossi & Mingos, 1974; Enemark & Feltham, 1974), can be adapted to this case much as Ryan & Eller (1976) have done for the case of transition-metal–sulfur dioxide complexes. For square-planar four-coordinate geometry this model predicts, upon extension to this case, a strongly bent Pt—S—O group and motion of the S atom off the axis of coordination in the direction of π coordination. The conformation with S—oxide axial may well allow more bending of the Pt—S—O group than would S—oxide equatorial. The twisting of the plane Pt—N—S relative to plane

Table 3. *Bond angles with e.s.d.'s in* Pt(*SR-methionine sulfoxide*)Cl_2 *hydrate*

See legend for Fig. 1 for explanation of computation of e.s.d.'s.

Cl(2)—Pt—Cl(1)	90·82 (9)°	O(3)—S—C(5)	108·9 (5)
Cl(1)—Pt—N	84·84 (20)	S—C(4)—C(3)	111·9 (7)
N—Pt—S	93·71 (20)	C(4)—C(3)—C(2)	114·0 (8)
S—Pt—Cl(2)	90·95 (9)	C(3)—C(2)—N	111·8 (7)
C(4)—S—C(5)	100·3 (5)	C(3)—C(2)—C(1)	115·5 (8)
Pt—S—O(3)	116·1 (3)	Pt—N—C(2)	123·2 (6)
Pt—S—C(5)	112·4 (4)	O(2)—C(1)—C(2)	123·5 (10)
Pt—S—C(4)	108·2 (3)	O(1)—C(1)—C(2)	113·5 (8)
C(4)—S—O(5)	109·7 (5)	O(2)—C(1)—C(1)	122·9 (10)

Cl—Pt—Cl (shown in Fig. 2) is consistent with this model. The sulfoxide O—Pt distance in this complex is 3·115 (6) Å. The Pt—S—O angle is 116·1 (3)°.

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trans-Bis[2-(di-*tert*-butylphosphinato)phenoxy]platinum(II)

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Abstract. $\{Pt[OC_6H_4P(C_4H_9)_2]_2\}$, $C_{28}H_{44}O_2P_2Pt$, triclinic, $P\bar{1}$; $a = 8{\cdot}60\,(1)$, $b = 11{\cdot}93\,(1)$, $c = 8{\cdot}03\,(1)$ Å, $\alpha = 94{\cdot}3\,(1)$, $\beta = 110{\cdot}5\,(1)$, $\gamma = 109{\cdot}1\,(1)°$; $Z = 1$, $D_x = 1{\cdot}56$ g cm^{-3}, $V = 712{\cdot}3$ Å^3. The centrosymmetric molecules contain two $\overline{\text{Pt—P—C—C—O}}$ chelate rings resulting from internal *O*-metallation and demethylation of 2-methoxyphenylphosphine ligands. Except for the *tert*-butyl substituents, all atoms of a molecule are coplanar to within the accuracy of the analysis.

Introduction. Cell dimensions were determined from zero-level precession and Weissenberg photographs [λ(Mo $K\alpha$) = 0·7107 Å] and intensities were recorded on Weissenberg photographs of reciprocal-lattice levels *hk*0–*hk*8. Visual estimation gave 2164 independent F_o which were not corrected for absorption. Solution of the structure was by the heavy-atom method and full-matrix least-squares refinement gave a final R of 12·0%. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974), and atomic coordinates, anisotropic temperature factors for Pt and P, and isotropic temperature factors for C and O were refined. The final atomic parameters with their e.s.d.'s are listed in Table 1.*

Discussion. Jones, Shaw & Turtle (1974) have shown that complexes of platinum(II) with 2-methoxyphenylphosphines undergo internal metallation of the methoxy substituent. According to the reaction conditions, there may be either metallation of the methyl C atom or demethylation and metallation of the O atom. This paper describes the structure of an *O*-metallated compound and the following paper that of a *C*-metallated compound.

The molecular structure and atom numbering are

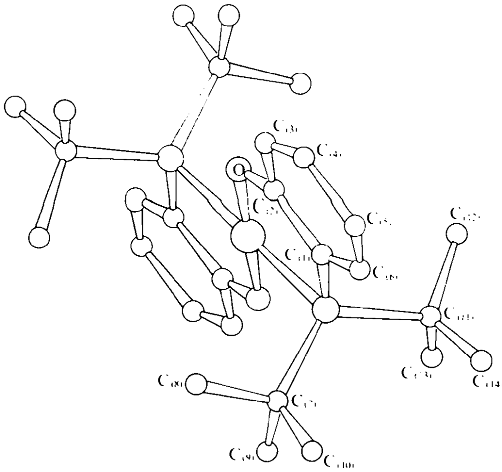

Fig. 1. The molecular structure and atom numbering.

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