Ni1—S7	2.1678 (12)	S6—C4	1.698 (4)
Ni1—S1	2.1761 (11)	S7—C4^{i}	1.698 (4)
S1—C1	1.734 (4)	C1—C2	1.353 (5)
S2—C2	1.727 (4)	C4—C4^{i}	1.435 (8)
S3—C3	1.718 (4)	N1—P1	1.583 (3)
S3—C1	1.746 (4)	N1—P2	1.585 (3)
S4—C3	1.731 (4)		
S6—Ni1—S2	177.65 (5)	C2—C1—S3	115.9 (3)
S6—Ni1—S7	90.91 (4)	S1—C1—S3	122.8 (2)
S2—Ni1—S7	87.45 (4)	C1—C2—S2	121.7 (3)
S6—Ni1—S1	88.24 (4)	C1—C2—S4	115.8 (3)
S2—Ni1—S1	93.46 (4)	S2—C2—S4	122.4 (2)
S7—Ni1—S1	177.88 (5)	S5—C3—S3	123.0 (3)
C1—S1—Ni1	101.64 (14)	S5—C3—S4	124.1 (3)
C2—S2—Ni1	101.92 (14)	S3—C3—S4	112.9 (2)
C3—S3—C1	97.7 (2)	C4^{i}—C4—S6	118.7 (4)
C3—S4—C2	97.6 (2)	C4^{i}—C4—S7^{i}	119.4 (4)
C4—S6—Ni1	105.76 (14)	S6—C4—S7^{i}	121.9 (2)
C4^{i}—S7—Ni1	105.17 (14)	P1—N1—P2	137.4 (2)
C2—C1—S1	121.2 (3)		

Symmetry code: (i) $-x, 1-y, -z$.

H atoms were placed geometrically and refined with a riding model, and with $U_{\rm iso}$ constrained to be $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Work at the Argonne National Laboratory is sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1185). Services for accessing these data are described at the back of the journal.

References

Bigoli, F., Deplano, P., Devillanova, F. A., Ferraro, J. R., Lippolis, V., Lukes, P. J., Mercuri, M. L., Pellinghelli, M. A., Trogu, E. F. & Williams, J. M. (1997). *Inorg. Chem.* **36**, 1218–1226.

Cassoux, P. & Valade, L. (1992). *Inorganic Materials*, edited by D. W. Bruce & D. O'Hare, pp. 1–58. Chichester, England: Wiley & Sons.

Cassoux, P., Valade, L., Kobayashi, H., Kobayashi, A., Clark, R. A. & Underhill, A. E. (1991). *Coord. Chem. Rev.* **110**, 115–160.

Deplano, P., Mercuri, M. L., Pintus, G. & Trogu, E. F. (1998). *Nickel Dithiolenes as Near-IR Dyes and Precursors of Sulfur-rich Donors*. XXXIIIth Int. Conf. Coord. Chem. August 30–September 4, Florence, Italy.

Olk, R.-M., Olk, B., Dietzsch, W., Kirmse, R. & Hoyer, E. (1992). *Coord. Chem. Rev.* **117**, 99–133.

Pullen, A. E., Olk, R.-M., Zeltner, S., Hoyer, E., Abboud, K. A. & Reynolds, J. R. (1997). *Inorg. Chem.* **36**, 958–959.

Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Programs*. Version 5.1. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA

Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA

Williams, J. M., Ferraro, J. R., Thorn, J. R., Carlson, K. D., Geiser, U., Wang, H. H., Kini, A. M. & Whangbo, M.-H. (1992). In *Organic Superconductors (Including Fullerenes)*. Englewood Cliffs, New Jersey, USA: Prentice Hall.

Acta Cryst. (1999). C**55**, 1255–1257

(L-2-Ammonio-4-methylsulfinylbutanoic acid-κ*S*)trichloroplatinum(II)–18-crown-6–water (1/1/2)

Clemens Bruhn, Olaf Gravenhorst, Christoph Wagner and Dirk Steinborn

Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle(Saale), Germany. E-mail: bruhn@chemie.uni-halle.de

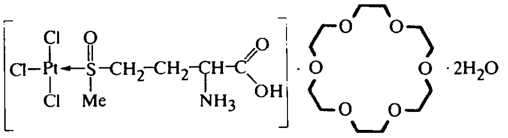
(*Received 18 January 1999; accepted 9 April 1999*)

Abstract

The structure of the title compound, $[\mathrm{Pt(C_5H_{12}NO_3S)Cl_3]\cdot C_{12}H_{24}O_6\cdot 2H_2O}$, was determined by single-crystal X-ray diffraction at 223 K. The metal complex $[\mathrm{PtCl_3}$(*S*-metoH$_2$)] consists of square-planar Pt$^{\rm II}$ coordinated with one *S*-bonded protonated L-methionine sulfoxide (metoH$_2$) and three chloro ligands. The ammonio group of the metoH$_2$ ligand forms three N—H···O hydrogen bonds to the crown ether 18-crown-6 [N···O 2.81 (2)–3.03 (3) Å]. The crystal structure consists of chains built up of these units connected by two water molecules *via* hydrogen bonds.

Comment

The anticancer activity of platinum compounds promoted investigations on platinum complexes with bioligands. Nowadays, attention is focused on Pt$^{\rm IV}$ complexes because of the lower toxicity and the possibility of oral administration (Keppler, 1993; Reedijk, 1992). In the course of our investigations on crown-ether-influenced ligand-exchange reactions in aquachloroplatinates (Steinborn, Junicke & Heinemann, 1997; Steinborn *et al.*, 1998), we found that aquapentachloroplatinic acid, $\mathrm{(H_3O)[PtCl_5(H_2O)]\cdot 2}$(18-cr-6)$\cdot$6H$_2$O (18-cr-6 is 18-crown-6) reacts with L-methionine sulfoxide (metoH). On reduction of Pt$^{\rm IV}$, several Pt$^{\rm II}$ complexes were formed and the title compound, [PtCl$_3$(*S*-metoH$_2$)]$\cdot$(18-cr-6)$\cdot$2H$_2$O, (I), was separated.



(I)

The molecular structure of (I) is shown along with the numbering scheme in Fig. 1. The complex crystallizes in space group $P2_1$. The crown ether molecule was found to be disordered over two sites (designated *a* and *b*),

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

which were both refined with anisotropic O and isotropic C positions. Their occupancy factors were first refined independently, were found to have approximately equal population and were finally fixed at 0.5.

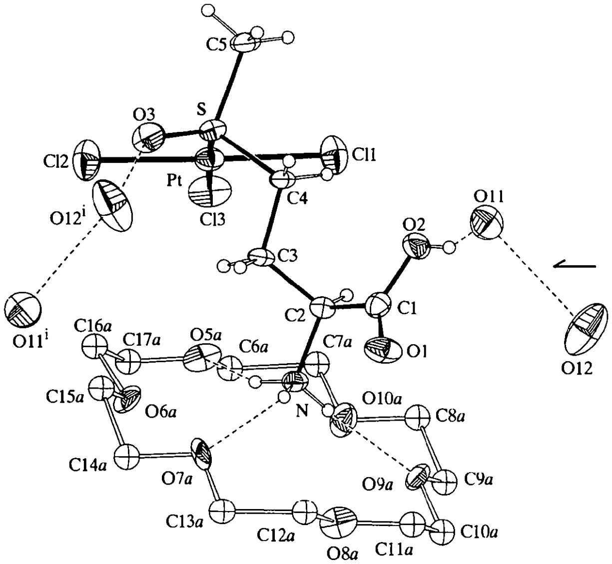


Fig. 1. The molecular structure of (I) displaying 30% probability displacement ellipsoids. Only the *a* position of the disordered crown ether molecule is shown. Isotropically refined atoms are either omitted or drawn as circles of arbitrary radii. Hydrogen bonds are shown as dashed lines.

The Pt atom is square-planar coordinated (sum of angles 360.0°) by one protonated *S*-bonded methionine sulfoxide and three chloro ligands. The Pt—Cl bond lengths are 2.263 (3)–2.323 (2) Å. The Pt—S bond length is 2.215 (2) Å and corresponds to the Pt—S distances in Pt^{II} complexes of dimethyl sulfoxide (2.174–2.261 Å, mean value 2.211 Å, number of data points n = 31; Allen & Kennard, 1993).

The ammonio group of the amino acid forms three N—H···O hydrogen bonds to the crown ether molecule. The N···O distances in the range 2.93 (2)–3.03 (3) Å, with a mean of 2.97 Å {2.81 (2)–2.98 (2) Å and mean value 2.89 Å; these values in braces refer to the *b* position of the disordered crown ether molecule}, are in the range typical for N—H···O hydrogen bonds (2.57–3.22 Å; Jeffrey & Saenger, 1994). In rough approximation, the crown ether has D_{3d} symmetry. The torsion angles (absolute values) are in the ranges 168 (2)–180 (2)° {165 (3)–180 (2)°} for C—O—C—C and 57 (2)–70 (2)° {43 (5)–63 (3)°} for O—C—C—O; the conformation of the macrocycle is characterized by an alternating sequence of the partial conformation of the OCCO subunits *ap*, *−sc*, *ap* and *ap*, *+sc*, *ap*. This conformation is in good agreement with that observed for $(H_3O)[PtCl_5(H_2O)]\cdot 2(18\text{-cr-}6)\cdot 6H_2O$ (Steinborn, Gravenhorst *et al.*, 1997) and for the hydrated crown ethers 18-cr-6·nH$_2$O (n = 4, 6, 8, 12; Mootz *et al.*, 1994; Albert & Mootz, 1997), but differs from that in unhydrated solid 18-cr-6 (Maverick *et al.*, 1980).

The crystal structure consists of chains built up of $[PtCl_3(metoH_2)]\cdot(18\text{-cr-}6)$ units connected by two water molecules *via* hydrogen bonds, such that the C(O)OH and S═O groups of the metoH$_2$ ligand act as hydrogen donor and acceptor, respectively, towards two water molecules (O11 and O12). The C(O)O2—H···O11 hydrogen bond is relatively short [O2···O11 2.561 (9) Å], whereas the O12—H···O3^i═S hydrogen bond seems to be weaker [O12···O3^i 2.97 (1) Å; symmetry code: (i) $2-x$, $\frac{1}{2}+y$, $1-z$]. The distance between the two water molecules [O11···O12 2.77 (1) Å] is the same as that in ice of the β-tridymite structure (Wells, 1984).

Experimental

The title complex was obtained by reaction of $(H_3O)[PtCl_5(H_2O)]\cdot 2(18\text{-cr-}6)\cdot 6H_2O$ with L-methionine sulfoxide in the molar ratio 1:3 in aqueous solution. The precipitate was filtered and the filtrate concentrated almost to dryness whereupon an oily residue or yellow crystals of (I) were obtained (yield *ca* 7%).

Crystal data

$[Pt(C_5H_{12}NO_3S)Cl_3]\cdot$-
$C_{12}H_{24}O_6\cdot 2H_2O$
M_r = 768.00
Monoclinic
$P2_1$
a = 9.019 (3) Å
b = 17.061 (4) Å
c = 9.458 (4) Å
β = 93.90 (4)°
V = 1452.0 (8) Å^3
Z = 2
D_x = 1.757 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 2000 reflections
θ = 2.26–25.00°
μ = 5.229 mm^{-1}
T = 223 (2) K
Block
0.30 × 0.20 × 0.20 mm
Yellow

Data collection

Stoe IPDS diffractometer with area detector
133 frames were taken oscillating the crystal 1.5°
Absorption correction: numerical (*XRED*; Stoe & Cie, 1996*b*)
T_{min} = 0.223, T_{max} = 0.351
10 675 measured reflections
2650 independent reflections (plus 2338 Friedel-related reflections)

4710 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 25°
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 12$
Mean intensity with 50 reflections per image
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
S = 1.071
4988 reflections
351 parameters

$\Delta\rho_{max}$ = 1.374 e Å^{-3}
$\Delta\rho_{min}$ = −1.295 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.012$
Absolute structure: Flack (1983)
Flack parameter = −0.010 (8)

Table 1. *Selected geometric parameters (Å, °)*

C1—O1	1.203 (9)	Cl3—Pt	2.323 (2)
C1—O2	1.317 (9)	Pt—S	2.215 (2)
C1—C2	1.521 (10)	O3—O12^{i}	2.966 (11)
C2—N	1.484 (8)	O11—O2	2.561 (9)
C2—C3	1.517 (10)	O11—O12	2.768 (12)
C3—C4	1.534 (8)	N—O5*A*	2.97 (2)
C4—S	1.781 (7)	N—O7*A*	3.03 (3)
C5—S	1.777 (7)	N—O9*A*	2.93 (2)
O3—S	1.450 (6)	N—O5*B*	2.98 (2)
Cl1—Pt	2.321 (3)	N—O7*B*	2.88 (3)
Cl2—Pt	2.263 (3)	N—O9*B*	2.81 (2)
O1—C1—O2	125.6 (7)	Cl2—Pt—Cl1	176.65 (12)
O1—C1—C2	123.2 (7)	O3—S—C5	109.0 (4)
O2—C1—C2	111.1 (6)	O3—S—C4	106.7 (4)
S—Pt—Cl1	90.48 (9)	C5—S—C4	101.9 (3)
S—Pt—Cl2	91.76 (10)	O3—S—Pt	119.8 (3)
S—Pt—Cl3	178.26 (9)	C5—S—Pt	108.2 (3)
Cl2—Pt—Cl3	89.81 (12)	C4—S—Pt	109.7 (2)
Cl1—Pt—Cl3	87.98 (10)		

Symmetry code: (i) $2 - x, \frac{1}{2} + y, 1 - z$.

Data collection: *IPDS Software* (Stoe & Cie, 1996*a*). Cell refinement: *IPDS Software*. Data reduction: *IPDS Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*93.

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged, as is the loan of chemicals by Degussa (Hanau).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1320). Services for accessing these data are described at the back of the journal.

References

Albert, A. & Mootz, D. (1997). *Z. Naturforsch. Teil B*, **52**, 615–619.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876-881.

Jeffrey, G. A. & Saenger, A. (1994). *Hydrogen Bonding in Biological Structures*, p. 29. Berlin: Springer.

Keppler, B. K. (1993). Editor. *Metal Complexes in Cancer Chemotherapy*. Weinheim: VCH.

Maverick, E., Seiler, P., Schweizer, W. B. & Dunitz, J. D. (1980). *Acta Cryst.* B**36**, 615–620.

Mootz, D., Albert, A., Schaefgen, S. & Stäben, D. (1994). *J. Am. Chem. Soc.* **116**, 12045–12046.

Reedijk, J. (1992). *Inorg. Chim. Acta*, **198–200**, 873–881.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Steinborn, D., Gravenhorst, O., Hartung, H. & Baumeister, U. (1997). *Inorg. Chem.* **36**, 2195–2199.

Steinborn, D., Gravenhorst, O., Junicke, H. & Heinemann, F. W. (1998). *Z. Naturforsch. Teil B*, **53**, 581-586.

Steinborn, D., Junicke, H. & Heinemann, F. W. (1997). *Inorg. Chim. Acta*, **256**, 87–92.

Stoe & Cie (1996*a*). *IPDS Software*. Version 2.86 (Stoe publication 4805–017). Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1996*b*). *XRED. Data Reduction Program*. Version 1.07. Stoe & Cie, Darmstadt, Germany.

Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., pp. 563–566. Oxford University Press.

Acta Cryst. (1999). C**55**, 1257–1260

Intramolecular C—H···O and intermolecular N—H···O and C—H···O interactions in *N*-ferrocenoylglycine benzyl ester, an effective dihydrogen phosphate anion sensing agent

John F. Gallagher, Peter T. M. Kenny and Michael J. Sheehy

School of Chemical Sciences, Dublin City University, Dublin 9, Ireland. E-mail: gallagherjfg@dcu.ie

(*Received 11 March 1999; accepted 12 April 1999*)

Abstract

The title compound, benzyl *N*-(ferrocenecarbonyl)glycinate, $[Fe(C_5H_5)(C_{15}H_{14}NO_3)]$, a glycine benzyl ester derivative, is an effective anion sensor for electrochemically sensing the dihydrogen phosphate anion ($H_2PO_4^-$). Intermolecular N—H···O hydrogen bonds form one-dimensional chains with graph set *C*(4) [N···O 2.811 (3) Å]. A two-dimensional network is formed by linking the chains through C_{ar}—H···O=C_{ester} interactions about inversion centres [graph set $R_2^2(14)$; C···O 3.406 (4) Å]. An intramolecular C_{Cp}—H···O=C_{ester} interaction [C···O 3.540 (3) Å] with graph set *S*(9) completes the hydrogen bonding.

Comment

The design of new redox-active ligands for application in diverse research areas such as medicinal chemistry and materials science has engrossed scientists in recent years. Ferrocene derivatives, which are efficient redox systems, have been studied extensively in charge-transfer chemistry, hydrogen-bonding and molecular-recognition science, peptide chemistry and non-linear optical materials (Moore *et al.*, 1993; Chesney *et al.*, 1998; Glidewell *et al.*, 1997; Degani & Heller, 1986; Kraatz *et al.*, 1997; Long, 1995). Anion recognition is