

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Racemic (RS_C, SR_S)-(2-[[1-allyloxy-carbonyl-3-(methylsulfonyl)propyl]-iminomethyl]phenyl- κ^3S, N, C^1)chlorido-platinum(II)

 Katsuhiro Isozaki,^{a*} Akira Sato^b and Kazushi Miki^{a,c}

^aOrganic Nanomaterials Center, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan, ^bMaterials Analysis Center, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan, and ^cApplied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Correspondence e-mail: isozaki.katsuhiro@nims.go.jp

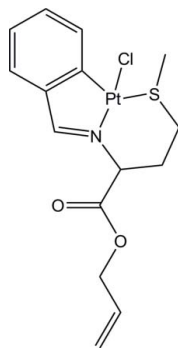
Received 10 October 2009; accepted 15 October 2009

Key indicators: single-crystal X-ray study; $T = 180$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.020; wR factor = 0.052; data-to-parameter ratio = 16.3.

The title compound, $[Pt(C_{15}H_{18}NO_2S)Cl]$, was obtained by the cyclometallation reaction of *cis*-bis(benzonitrile)dichlorido-platinum(II) with *N*-benzylidene-*L*-methionine allyl ester in refluxing toluene. The Pt^{II} atom has a square-planar geometry and is tetra-coordinated by the Cl atom and the C, N and S atoms from the benzylidene methionine ester ligand. In the crystal structure, the S atoms show opposite chiral configurations with respect to the α -carbon of the methionine, reducing steric repulsion between the methyl and allyl ester groups.

Related literature

For cyclometallated Pt^{II} complexes having terdentate benzylideneamine ligands cyclometallated benzylideneamine, see: Capapé *et al.* (2005); Caubet *et al.* (2003); Riera *et al.* (2000). For organometallic amino acid complexes, see: Severin *et al.* (1998).



Experimental

Crystal data

$[Pt(C_{15}H_{18}NO_2S)Cl]$
 $M_r = 506.90$
 Monoclinic, $P2_1/n$
 $a = 8.6000$ (13) Å
 $b = 9.5093$ (14) Å
 $c = 19.679$ (3) Å
 $\beta = 94.398$ (2)°

$V = 1604.6$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 9.04$ mm⁻¹
 $T = 180$ K
 $0.50 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
 $T_{min} = 0.610$, $T_{max} = 0.862$

12273 measured reflections
 3105 independent reflections
 2854 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.052$
 $S = 1.07$
 3105 reflections

191 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 1.36$ e Å⁻³
 $\Delta\rho_{min} = -0.48$ e Å⁻³

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

This work was supported financially by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientists (Start-up, 19850030).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2471).

References

- Bruker (2003). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Capapé, A., Crespo, M., Granell, J., Font-Bardía, M. & Solans, X. (2005). *J. Organomet. Chem.* **690**, 4309–4318.
 Caubet, A., López, C., Solans, X. & Font-Bardía, M. (2003). *J. Organomet. Chem.* **669**, 164–171.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Riera, X., Caubet, A., Lopez, C., Moreno, V., Solans, X. & Font-Bardía, M. (2000). *Organometallics*, **19**, 1384–1390.
 Severin, K., Bergs, R. & Beck, W. (1998). *Angew. Chem. Int. Ed.* **37**, 1634–1654.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2009). E65, m1401 [doi:10.1107/S160053680904238X]

Racemic (RS_C,SR_S)-(2-{[1-allyloxycarbonyl-3-(methylsulfanyl)propyl]iminomethyl}phenyl-κ³S,N,C¹)chloridoplatinum(II)

K. Isozaki, A. Sato and K. Miki

Comment

Research on cyclometallated complexes (Capapé *et al.*, 2005; Riera *et al.*, 2000) has been focused because of their fundamental applications as luminescent materials (Caubet *et al.*, 2003) and catalysts for a range of cross-coupling reactions. Amino acids, possessing natural chiral backbone and strong coordinating groups, are one of the potent candidates for designing stable cyclometallated complexes with highly controlled stereo-structure (Severin *et al.*, 1998). Here, we report the crystal structure of the platinum (II) complex (**1**), containing chiral methionine-derived C,N,S-terdentate ligand.

The crystal structure of title compound (**1**) is presented in Fig. 1. The Pt(II) atom is tetracoordinated in a square-planar environment by a Cl atom and C, N, S atoms from benzylidene methionine ester ligand. In the [Pt (C₁₅H₁₈NO₂S)Cl] (**1**), S atoms showed opposite chiral configurations to the α-carbon of methionine for reducing steric repulsion between methyl and allyl ester groups (Fig. 2).

Experimental

The methionine-derived ligand was synthesized from three step reactions, esterification, deprotection, condensation using Fmoc-*L*-methionine as a starting material (Fig. 3). A suspension of *cis*-[PtCl₂(PhCN)₂] and methionine-derived ligand was refluxed under nitrogen atmosphere for 3 h. The crude mixture was purified by SiO₂ flash column chromatography. Single crystals for X-ray analyses were obtained from a CH₂Cl₂ solution.

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C_{arene}—H and C_{allyl}—H = 0.93 Å, C_{methyl}—H = 0.96 Å, C_{alkyl}—H = 0.97 Å and C_α—H = 0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{arene}}, \text{C}_{\text{alkyl}})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. Electron density synthesis with coefficients $F_o - F_c$: Highest peak 1.36 at 0.0428, 0.4390, 0.1909 (0.86 Å from Pt1)

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3105 independent reflections
Radiation source: fine-focus sealed tube	2854 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.024$
$T = 180$ K	$\theta_{\text{max}} = 26.0^\circ$
ω scans	$\theta_{\text{min}} = 2.4^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$h = -9 \rightarrow 10$
$T_{\text{min}} = 0.610$, $T_{\text{max}} = 0.862$	$k = -11 \rightarrow 11$
12273 measured reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.020$	H-atom parameters constrained
$wR(F^2) = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.6405P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
3105 reflections	$(\Delta/\sigma)_{\text{max}} = 0.003$
191 parameters	$\Delta\rho_{\text{max}} = 1.36 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.456604 (14)	0.848674 (12)	0.309063 (6)	0.01942 (6)
S4	0.63428 (10)	0.87893 (9)	0.22448 (5)	0.02394 (18)
Cl1	0.60649 (11)	1.00955 (10)	0.37235 (5)	0.0338 (2)
C3	0.3033 (4)	0.8222 (3)	0.37990 (18)	0.0224 (7)
N4	0.3141 (3)	0.7078 (3)	0.26035 (14)	0.0222 (6)

supplementary materials

C6	0.1849 (5)	0.9473 (5)	-0.0659 (2)	0.0518 (12)
H6A	0.1530	0.8793	-0.0980	0.062*
H6B	0.2203	1.0341	-0.0801	0.062*
O7	0.1383 (4)	0.8499 (3)	0.16257 (16)	0.0423 (7)
C9	0.2011 (4)	0.6636 (3)	0.29340 (19)	0.0258 (8)
H9	0.1318	0.5959	0.2752	0.031*
C11	0.1695 (5)	0.8600 (4)	0.4821 (2)	0.0331 (9)
H11	0.1639	0.9067	0.5234	0.040*
O12	0.2371 (3)	0.7266 (3)	0.07819 (13)	0.0377 (6)
C13	0.1798 (5)	0.9200 (5)	0.0011 (3)	0.0497 (11)
H13	0.2122	0.9893	0.0324	0.060*
C15	0.1855 (4)	0.7230 (3)	0.36017 (17)	0.0242 (7)
C16	0.5768 (4)	0.7677 (4)	0.15222 (17)	0.0277 (7)
H16A	0.5139	0.8229	0.1190	0.033*
H16B	0.6699	0.7388	0.1311	0.033*
C17	0.2223 (4)	0.7597 (4)	0.14303 (18)	0.0292 (8)
C18	0.0640 (4)	0.6922 (4)	0.40057 (19)	0.0322 (8)
H18	-0.0100	0.6246	0.3868	0.039*
C19	0.2922 (4)	0.8882 (4)	0.44249 (18)	0.0274 (7)
H19	0.3685	0.9524	0.4580	0.033*
C20	0.0548 (4)	0.7633 (4)	0.46131 (18)	0.0366 (9)
H20	-0.0277	0.7465	0.4881	0.044*
C21	0.1259 (5)	0.7871 (5)	0.0261 (2)	0.0469 (11)
H21A	0.1100	0.7217	-0.0116	0.056*
H21B	0.0264	0.8009	0.0453	0.056*
C27	0.8092 (4)	0.7906 (4)	0.2577 (2)	0.0355 (9)
H27A	0.7881	0.6922	0.2627	0.053*
H27B	0.8434	0.8298	0.3012	0.053*
H27C	0.8892	0.8029	0.2268	0.053*
C28	0.3198 (4)	0.6605 (3)	0.18980 (18)	0.0246 (8)
H28	0.2675	0.5689	0.1867	0.030*
C29	0.4852 (4)	0.6366 (3)	0.16894 (19)	0.0270 (8)
H29A	0.5436	0.5870	0.2056	0.032*
H29B	0.4793	0.5756	0.1293	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.01859 (9)	0.02131 (9)	0.01877 (9)	-0.00125 (4)	0.00404 (6)	-0.00029 (4)
S4	0.0227 (4)	0.0254 (4)	0.0247 (5)	0.0004 (3)	0.0077 (3)	0.0000 (3)
Cl1	0.0320 (5)	0.0411 (5)	0.0291 (5)	-0.0148 (4)	0.0066 (4)	-0.0086 (4)
C3	0.0202 (18)	0.0253 (16)	0.0217 (18)	-0.0021 (13)	0.0012 (14)	0.0065 (13)
N4	0.0247 (15)	0.0216 (14)	0.0206 (14)	-0.0022 (11)	0.0042 (11)	-0.0008 (11)
C6	0.046 (3)	0.062 (3)	0.050 (3)	0.009 (2)	0.020 (2)	0.018 (2)
O7	0.0392 (17)	0.0494 (18)	0.0387 (17)	0.0171 (13)	0.0061 (14)	0.0016 (12)
C9	0.0243 (19)	0.0242 (18)	0.029 (2)	-0.0058 (13)	0.0012 (15)	-0.0004 (13)
C11	0.030 (2)	0.047 (2)	0.022 (2)	-0.0010 (16)	0.0050 (16)	-0.0026 (15)
O12	0.0289 (14)	0.0599 (18)	0.0244 (13)	0.0047 (13)	0.0030 (11)	0.0035 (12)

C13	0.036 (2)	0.052 (3)	0.062 (3)	0.007 (2)	0.005 (2)	0.001 (2)
C15	0.0224 (17)	0.0290 (18)	0.0211 (17)	-0.0015 (13)	0.0013 (13)	0.0021 (13)
C16	0.0244 (18)	0.036 (2)	0.0236 (17)	0.0017 (15)	0.0079 (14)	-0.0030 (15)
C17	0.0224 (18)	0.037 (2)	0.0287 (19)	-0.0002 (15)	0.0044 (14)	0.0039 (16)
C18	0.024 (2)	0.042 (2)	0.030 (2)	-0.0109 (16)	0.0030 (15)	0.0034 (17)
C19	0.0253 (19)	0.0330 (18)	0.0240 (18)	-0.0018 (15)	0.0021 (14)	-0.0021 (15)
C20	0.028 (2)	0.059 (3)	0.0234 (19)	-0.0062 (18)	0.0097 (15)	0.0058 (17)
C21	0.036 (2)	0.071 (3)	0.033 (2)	0.000 (2)	-0.0041 (18)	0.009 (2)
C27	0.0222 (19)	0.043 (2)	0.041 (2)	0.0063 (16)	0.0015 (16)	-0.0047 (18)
C28	0.029 (2)	0.0233 (18)	0.0219 (18)	-0.0019 (13)	0.0018 (15)	-0.0044 (12)
C29	0.027 (2)	0.0287 (18)	0.0255 (19)	0.0064 (14)	0.0037 (15)	-0.0075 (14)

Geometric parameters (Å, °)

Pt1—C3	2.006 (4)	C13—C21	1.446 (7)
Pt1—N4	2.009 (3)	C13—H13	0.9300
Pt1—C11	2.3037 (9)	C15—C18	1.392 (5)
Pt1—S4	2.3618 (9)	C16—C29	1.524 (5)
S4—C27	1.801 (4)	C16—H16A	0.9700
S4—C16	1.810 (3)	C16—H16B	0.9700
C3—C19	1.392 (5)	C17—C28	1.524 (5)
C3—C15	1.417 (5)	C18—C20	1.381 (5)
N4—C9	1.281 (4)	C18—H18	0.9300
N4—C28	1.464 (4)	C19—H19	0.9300
C6—C13	1.348 (6)	C20—H20	0.9300
C6—H6A	0.9300	C21—H21A	0.9700
C6—H6B	0.9300	C21—H21B	0.9700
O7—C17	1.204 (4)	C27—H27A	0.9600
C9—C15	1.446 (5)	C27—H27B	0.9600
C9—H9	0.9300	C27—H27C	0.9600
C11—C19	1.386 (5)	C28—C29	1.528 (5)
C11—C20	1.387 (5)	C28—H28	0.9800
C11—H11	0.9300	C29—H29A	0.9700
O12—C17	1.330 (4)	C29—H29B	0.9700
O12—C21	1.464 (5)		
C3—Pt1—N4	80.72 (13)	O7—C17—O12	125.4 (3)
C3—Pt1—C11	94.46 (10)	O7—C17—C28	124.4 (3)
N4—Pt1—C11	175.18 (8)	O12—C17—C28	110.1 (3)
C3—Pt1—S4	179.20 (10)	C20—C18—C15	119.1 (3)
N4—Pt1—S4	98.56 (8)	C20—C18—H18	120.4
C11—Pt1—S4	86.26 (3)	C15—C18—H18	120.4
C27—S4—C16	100.53 (18)	C11—C19—C3	121.2 (3)
C27—S4—Pt1	104.77 (14)	C11—C19—H19	119.4
C16—S4—Pt1	109.27 (12)	C3—C19—H19	119.4
C19—C3—C15	116.5 (3)	C18—C20—C11	119.6 (3)
C19—C3—Pt1	130.7 (3)	C18—C20—H20	120.2
C15—C3—Pt1	112.8 (2)	C11—C20—H20	120.2
C9—N4—C28	117.6 (3)	C13—C21—O12	111.9 (4)
C9—N4—Pt1	115.8 (2)	C13—C21—H21A	109.2

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C28—N4—Pt1	126.4 (2)	O12—C21—H21A	109.2
C13—C6—H6A	120.0	C13—C21—H21B	109.2
C13—C6—H6B	120.0	O12—C21—H21B	109.2
H6A—C6—H6B	120.0	H21A—C21—H21B	107.9
N4—C9—C15	117.4 (3)	S4—C27—H27A	109.5
N4—C9—H9	121.3	S4—C27—H27B	109.5
C15—C9—H9	121.3	H27A—C27—H27B	109.5
C19—C11—C20	121.1 (4)	S4—C27—H27C	109.5
C19—C11—H11	119.4	H27A—C27—H27C	109.5
C20—C11—H11	119.4	H27B—C27—H27C	109.5
C17—O12—C21	118.2 (3)	N4—C28—C17	109.0 (3)
C6—C13—C21	122.5 (5)	N4—C28—C29	113.6 (3)
C6—C13—H13	118.8	C17—C28—C29	114.2 (3)
C21—C13—H13	118.8	N4—C28—H28	106.5
C18—C15—C3	122.4 (3)	C17—C28—H28	106.5
C18—C15—C9	124.2 (3)	C29—C28—H28	106.5
C3—C15—C9	113.3 (3)	C16—C29—C28	116.4 (3)
C29—C16—S4	115.0 (2)	C16—C29—H29A	108.2
C29—C16—H16A	108.5	C28—C29—H29A	108.2
S4—C16—H16A	108.5	C16—C29—H29B	108.2
C29—C16—H16B	108.5	C28—C29—H29B	108.2
S4—C16—H16B	108.5	H29A—C29—H29B	107.4
H16A—C16—H16B	107.5		
N4—Pt1—S4—C27	-107.41 (16)	C21—O12—C17—C28	165.9 (3)
C11—Pt1—S4—C27	72.70 (14)	C3—C15—C18—C20	1.8 (6)
C11—Pt1—S4—C16	179.70 (13)	C9—C15—C18—C20	-175.2 (3)
N4—Pt1—C3—C19	-176.3 (4)	C20—C11—C19—C3	1.1 (6)
C11—Pt1—C3—C19	3.6 (3)	C15—C3—C19—C11	-1.6 (5)
N4—Pt1—C3—C15	1.1 (2)	Pt1—C3—C19—C11	175.8 (3)
C11—Pt1—C3—C15	-179.0 (2)	C15—C18—C20—C11	-2.4 (6)
C3—Pt1—N4—C9	-1.8 (3)	C19—C11—C20—C18	1.0 (6)
S4—Pt1—N4—C9	178.5 (2)	C6—C13—C21—O12	128.9 (4)
C3—Pt1—N4—C28	172.9 (3)	C17—O12—C21—C13	90.1 (5)
S4—Pt1—N4—C28	-6.8 (3)	C9—N4—C28—C17	86.9 (4)
C28—N4—C9—C15	-173.0 (3)	Pt1—N4—C28—C17	-87.7 (3)
Pt1—N4—C9—C15	2.2 (4)	C9—N4—C28—C29	-144.4 (3)
C19—C3—C15—C18	0.1 (5)	Pt1—N4—C28—C29	40.9 (4)
Pt1—C3—C15—C18	-177.7 (3)	O7—C17—C28—N4	-9.1 (5)
C19—C3—C15—C9	177.5 (3)	O12—C17—C28—N4	174.3 (3)
Pt1—C3—C15—C9	-0.3 (4)	O7—C17—C28—C29	-137.4 (4)
N4—C9—C15—C18	176.1 (3)	O12—C17—C28—C29	46.0 (4)
N4—C9—C15—C3	-1.2 (4)	S4—C16—C29—C28	69.7 (4)
C27—S4—C16—C29	83.2 (3)	N4—C28—C29—C16	-78.1 (4)
Pt1—S4—C16—C29	-26.7 (3)	C17—C28—C29—C16	47.8 (4)
C21—O12—C17—O7	-10.6 (6)		

Fig. 1

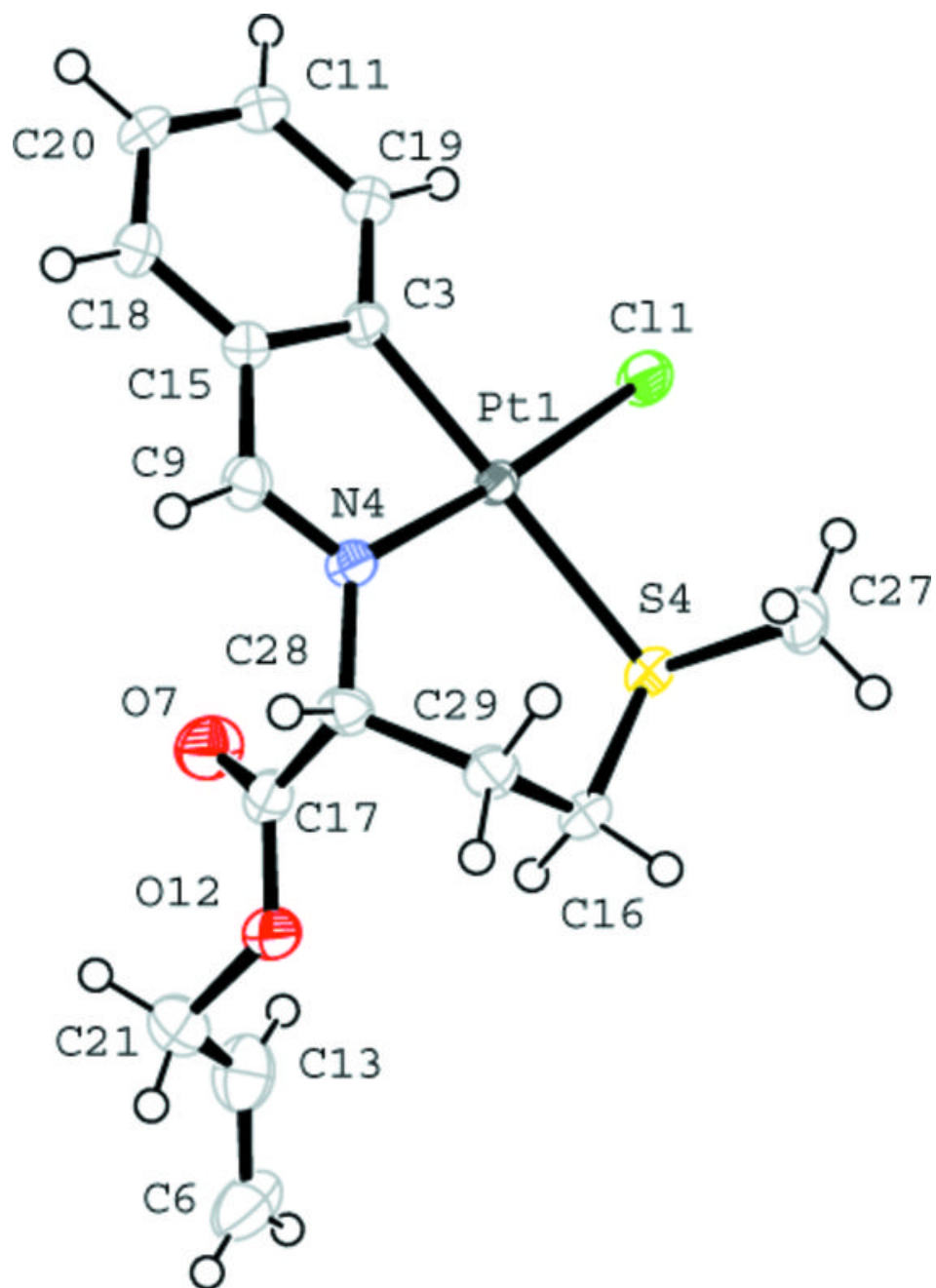


Fig. 2

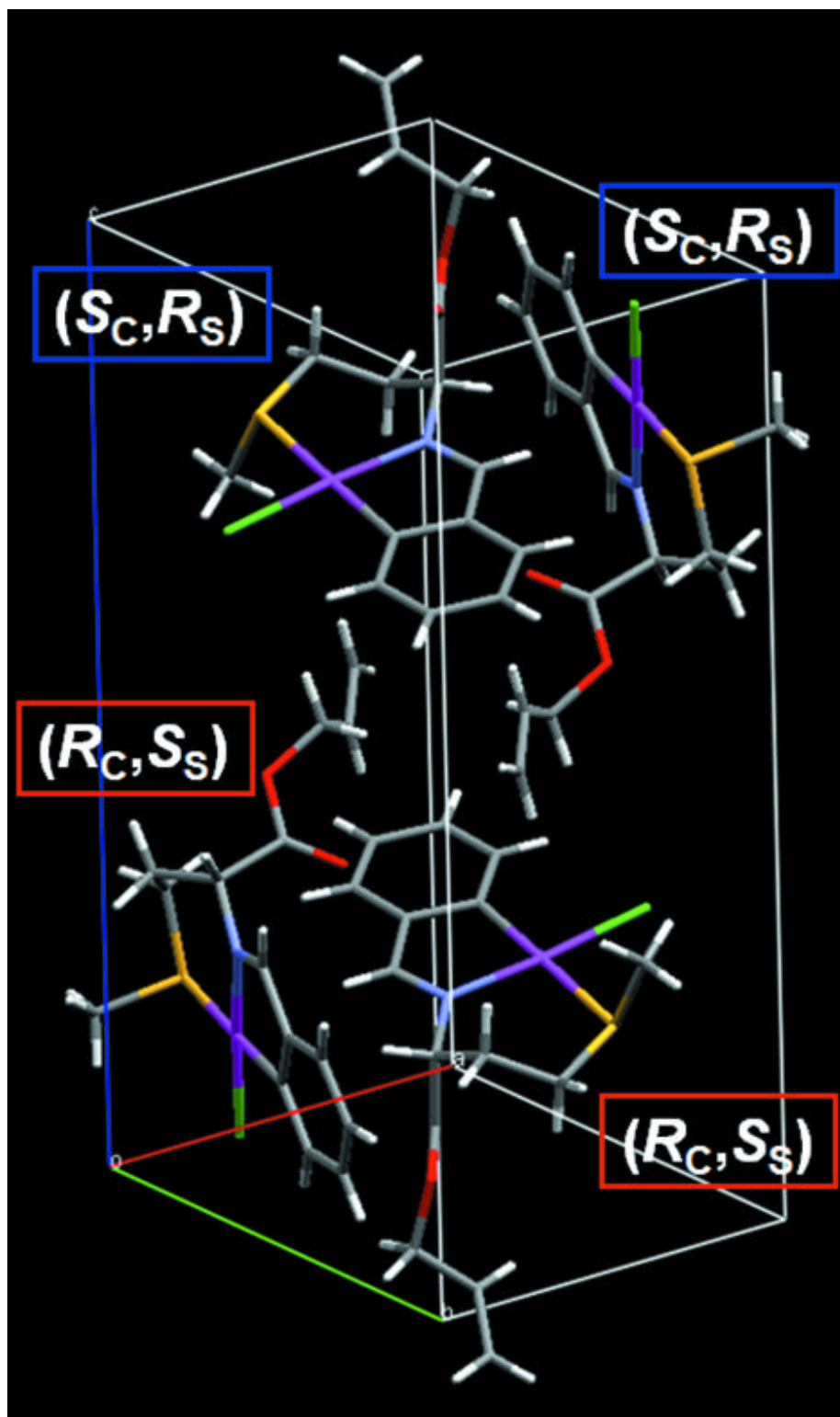


Fig. 3

