Supporting Information

Epitaxial Retrieval of a Disappearing Polymorph

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Experimental crystallographic tables

For all structures: \( Z = 4 \); experiments were carried out at 293 K with Mo \( K \alpha \) radiation using a SuperMova, single source at offset, Eos diffractometer; numerical absorption corrections based on Gaussian integration over multifaceted crystal models were implemented using various versions of CrysAlisPro software;\(^1\) structures were solved using SHELXS\(^2\) and refined using SHELXL\(^2\) in Olex2;\(^3\) H-atom parameters were constrained. For the refinement of \( \gamma-1 \), two distance restraints (DFIX) were required on the macrocycle to obtain more sensible C-C distances.

| Chemical formula         | \( \alpha-1 \)         | \( \beta-1 \)         | \( \gamma-1 \)         |
|--------------------------|------------------------|------------------------|------------------------|
| \( \text{C}_6\text{H}_{12}\text{Cl}_2\text{OPdS}_2 \) |                         |                         |                         |
| \( M_r \)                | 341.58                 | 341.58                 | 341.58                 |
| Crystal system, space group | Monoclinic, \( P2_1/n \) | Monoclinic, \( P2_1/c \) | Monoclinic, \( P2_1/n \) |
| \( a \) (\( \text{Å} \)) | 8.4502 (4)             | 9.3384(3)              | 7.02123(16)            |
| \( b \) (\( \text{Å} \)) | 12.1807(5)             | 12.6575(4)             | 11.4020(3)             |
| \( c \) (\( \text{Å} \)) | 10.3745(4)             | 9.0498(3)              | 13.3817(3)             |
| \( \beta \) (\( ^\circ \)) | 105.125(4)             | 92.260(3)              | 96.785(2)              |
| \( V \) (\( \text{Å}^3 \)) | 1030.85(8)             | 1068.87(6)             | 1063.78(5)             |
| \( Z \)                  | 4                      | 4                      | 4                      |
| Radiation type           | Mo \( K \alpha \)      | Mo \( K \alpha \)      | Mo \( K \alpha \)      |
| \( \mu \) (\( \text{mm}^{-1} \)) | 2.67                   | 2.58                   | 2.59                   |
| Crystal size (\( \text{mm} \)) | 0.22 \times 0.10 \times 0.03 | 0.15 \times 0.12 \times 0.10 | 0.11 \times 0.10 \times 0.02 |

**Data collection**

Software

|                | CrysAlis\(^{\text{Pro}}\), Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171.NET) (compiled Aug 2 2013:16:46:58) | CrysAlis\(^{\text{Pro}}\), Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171.NET) (compiled Aug 2 2013:16:46:58) | CrysAlis\(^{\text{Pro}}\), Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171.NET) (compiled Aug 2 2013:16:46:58) |
|----------------|--------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| \( T_{	ext{min}}, T_{	ext{max}} \)                                 | 0.721, 1.000                                                               | 0.781, 0.914                                                               | 0.883, 1.000                                                               |
| No. of measured, independent and observed \( [I > 2\sigma(I)] \) reflections | 4597, 2281, 1633                                                          | 4391, 2341, 1789                                                          | 7692, 2390, 1782                                                          |
| \( R_{	ext{int}} \)                                               | 0.051                                                                      | 0.033                                                                      | 0.053                                                                      |
| \( \langle \sin \theta /\lambda \rangle_{\text{max}} \) (\( \text{Å}^{-1} \)) | 0.664                                                                      | 0.661                                                                      | 0.662                                                                      |

**Refinement**

| \( R(F^2 > 2\sigma(F^2)), wR(F^2), S \)                  | 0.048, 0.094, 1.04                                      | 0.038, 0.075, 1.00                                      | 0.037, 0.084, 1.05                                      |
| No. of reflections                                    | 2281                                                       | 2341                                                       | 2390                                                       |
| No. of parameters                                    | 109                                                        | 109                                                        | 109                                                        |
| No. of restraints                                    | 0                                                          | 0                                                          | 2                                                          |
| \( \Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \) (e \( \text{Å}^{-3} \)) | 0.95, −0.78                                               | 0.60, −0.57                                               | 0.62, −0.96                                               |
### Crystal data

|                | α-2                      | β-2                      | β-1-epitaxy            |
|----------------|--------------------------|--------------------------|------------------------|
| **Chemical formula** | C_6H_{12}Cl_2OPtS_2       | C_6H_{12}Cl_2OPtS_2      | C_6H_{12}Cl_2OPdS_2    |
| **M_r**        | 430.27                   | 430.27                   | 341.58                 |
| **Crystal system, space group** | Monoclinic, P2_1/n | Monoclinic, P2_1/c | Monoclinic, P2_1/c |
| a (Å)          | 8.45248(18)              | 9.4166(18)               | 9.3451(4)              |
| b (Å)          | 12.2690(2)               | 12.6646(2)               | 12.6701(5)             |
| c (Å)          | 10.3536(2)               | 9.03759(16)              | 9.0724(4)              |
| β (°)          | 105.542(2)               | 91.5297(17)              | 92.424(4)              |
| V (Å³)         | 1034.45(4)               | 1077.43(3)               | 1073.25(8)             |
| Z              | 4                        | 4                        | 4                      |
| **Radiation type** | Mo Kα                   | Mo Kα                   | Mo Kα                 |
| μ (mm⁻¹)       | 14.43                    | 13.86                    | 2.57                   |
| **Crystal size (mm)** | 0.08 × 0.07 × 0.05       | 0.11 × 0.04 × 0.02       | 0.12 × 0.07 × 0.05     |

### Data collection

| Software | CrysAlisPRO, Agilent Technologies, Version 1.171.37.31 (release 14-01-2014 CrysAlis171 .NET) (compiled Jan 14 2014,18:38:05) | CrysAlisPRO, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) | CrysAlisPRO, Agilent Technologies, Version 1.171.36.28 (release 01-02-2013 CrysAlis171 .NET) (compiled Feb 1 2013,16:14:44) |
|----------|-----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|
| T_min, T_max | 0.471, 0.626                                                                                                    | 0.460, 0.750                                                                                                    | 0.821, 0.961                                                                                                    |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 3879, 2260, 2004                                                                                               | 4083, 2346, 2152                                                                                               | 3628, 2313, 1875                                                                                               |
| R_int    | 0.028                                                                                                           | 0.012                                                                                                           | 0.023                                                                                                           |
| (sin θ/λ)_{max} (Å⁻¹) | 0.662                                                                                                        | 0.663                                                                                                        | 0.662                                                                                                        |

### Refinement

| R(F² > 2σ(F²)), wR(F²), S | 0.030, 0.070, 1.02 | 0.015, 0.037, 1.06 | 0.033, 0.067, 1.03 |
|---------------------------|-------------------|-------------------|-------------------|
| No. of reflections        | 2260              | 2346              | 2313              |
| No. of parameters         | 110               | 109               | 109               |
| No. of restraints         | 0                 | 0                 | 0                 |
| Δρ_{max}, Δρ_{min} (e Å⁻³) | 0.99, −2.02       | 0.72, −0.42       | 0.48, −0.56       |
Geometry optimization results

**Table A1.** Calculated values of selected structural parameters and their deviation from experimentally obtained values.

| Calculated structural parameters /Å | Deviation from experimental value/% |
|------------------------------------|-------------------------------------|
| α-1 | α-2 | β-1 | β-2 | γ-1 | “γ-2” | α-1 | α-2 | β-1 | β-2 | γ-1 | “γ-2” |
|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|------|
| M-Cl1 | 2.35 | 2.36 | 2.34 | 2.34 | 2.33 | −1.0 | −1.3 | −1.2 | −0.8 | −1.4 | n/a |
| M-Cl2 | 2.35 | 2.36 | 2.34 | 2.34 | 2.34 | −0.9 | −1.4 | −0.8 | −0.6 | −0.7 | n/a |
| M-S4 | 2.26 | 2.24 | 2.27 | 2.25 | 2.26 | 0.2 | 0.2 | 0.0 | 0.0 | −0.1 | n/a |
| M-S7 | 2.26 | 2.24 | 2.27 | 2.25 | 2.26 | −0.2 | 0.0 | −0.4 | 0.2 | 0.3 | n/a |

**Table A2.** Calculated values for the lattice parameters and their percentage deviation from experimentally obtained values.

| Calculated lattice parameters | Deviation from experimental value/% |
|-------------------------------|-------------------------------------|
| a (Å)                        | 8.547 | 8.544 | 9.514 | 9.468 | 7.012 | −1.1 | −1.1 | −1.0 | −1.4 | 0.1 |
| b (Å)                        | 12.34 | 12.223 | 12.625 | 12.715 | 11.471 | −0.6 | −0.3 | 0.3 | −0.5 | −0.6 |
| c (Å)                        | 10.331 | 10.367 | 8.947 | 8.914 | 13.395 | 0.2 | 0.1 | 1.0 | 1.5 | −0.1 |
| β (°)                        | 106.29 | 105.64 | 90.73 | 91.25 | 96.96 | −0.7 | −0.5 | 0.9 | 1.1 | −0.2 |
| V(Å³)                       | 1045.95 | 1042.58 | 1074.52 | 1072.95 | 1069.58 | −1.1 | −1.1 | 0.3 | −0.4 | −0.5 |

Unit cell parameters obtained for hypothetical “γ-2” are as $a = 6.964$, $b = 11.757$, $c = 13.273$ Å, $β = 97.507°$ and $V = 1077.34$ Å³.
Table A3. Average partial atomic charges (in a.u.) derived from the Mulliken population analysis (C atoms omitted).

| Phase | M  | O  | Cl  | S   | H  |
|-------|----|----|-----|-----|----|
| α-1   | 0.66 | −0.49 | −0.48 | 0.34 | 0.25 |
| β-1   | 0.65 | −0.52 | −0.465 | 0.33 | 0.25 |
| γ-1   | 0.72 | −0.49 | −0.48 | 0.325 | 0.24 |
| α-2   | 0.33 | −0.49 | −0.435 | 0.385 | 0.26 |
| β-2   | 0.32 | −0.52 | −0.425 | 0.375 | 0.26 |
| “γ-2” | 0.36 | −0.49 | −0.435 | 0.37 | 0.26 |

Crystal structures

Structure of α-1

Crystals of α-1 were readily obtained as orange blocks by diffusion of Et₂O vapor into a solution of 1 in MeNO₂ at room temperature. They were also recovered from recrystallizations carried out at 30 and 35 °C.

The structure of α-1 has been previously described.⁴ The complex crystallizes in monoclinic space group $P2_1/n$ with $a = 8.4502(4)$, $b = 12.1807(5)$, $c = 10.3745(4)$ Å, $β = 105.125(4)^\circ$ and $V = 1030.85(8)$ Å³. The Pd(II) center is bound in a [4+1] square based pyramidal coordination environment containing a cis-Cl₂S₂ equatorial plane with the macrocycle adopting a facially bound, endodentate conformation with respect to the oxygen donor and the ligand conformation is assigned as [234] following Dale analysis⁵ with corners at C3, C6 and C8 (Fig. A1; Table A4). This affords a distant, apically located O donor atom interacting with the metal center; the Pd···O distance of 2.958(4) Å lies within the sum of the relevant van der Waals radii [3.15 Å].⁶ The metal center is located slightly [0.0128(10) Å] out of the equatorial plane in the direction
opposite from the apical oxygen. The molecules pack into dimeric units about an inversion center such that the Pd center in one molecule rests over the Pd1–S7 bond of another (Table A5), with a perpendicular separation of 3.6247(2) Å between the PdCl₂S₂ least-squares planes. These dimers can then be considered as packing in ABAB alternating sheets in the bc plane, giving rise to a herringbone-like pattern when viewed parallel to the a axis (Fig. A2).

Figure A1. View of the experimentally determined structure of [PdCl₂([9]aneS₂O)] in α-1. Displacement ellipsoids are drawn at 50 % probability.
### Table A4. Coordination environment and macrocycle conformation for α-1

| Bond Length /Å | Bond Angle /° | Torsion Angle /° |
|----------------|---------------|-----------------|
| Pd1-Cl1        | 2.328(2)      | Cl1-Pd1-Cl2     | 93.06(6)       |
|                |               | O1-C2-C3-S4     | 44.9(6)        |
| Pd1-Cl2        | 2.329(2)      | Cl2-Pd1-S7      | 88.52(7)       |
|                |               | C2-C3-S4-C5     | 44.2(2)        |
| Pd1-S4         | 2.265(2)      | S7-Pd1-S4       | 90.25(6)       |
|                |               | C3-S4-C5-C6     | −125.4(5)      |
| Pd1-S7         | 2.255(2)      | S4-Pd1-Cl1      | 88.17(6)       |
|                |               | S4-C5-C6-S7     | 31.1(7)        |
| Pd1···O1       | 2.958(4)      | Cl1-Pd1-S7      | 177.90(7)      |
|                |               | C5-C6-S7-C8     | 81.9(6)        |
|                |               | Cl2-Pd1-S4      | 178.77(6)      |
|                |               | C6-S7-C8-C9     | −51.6(5)       |
|                |               | S7-C8-C9-O1     | −51.2(7)       |
|                |               | C8-C9-O1-C2     | 143.4(5)       |
|                |               | C9-O1-C2-C3     | −130.1(5)      |

### Table A5. Inter-dimer geometry for α-1

| Atomic Distance /Å | Angle /° |
|--------------------|----------|
| Pd1-Cl1#           | 5.039(2) |
| Pd1-Cl2#           | 4.504(2) |
| Pd1-S4#            | 4.345(2) |
| Pd1-S7#            | 3.794(2) |
| Pd1-Pd1#           | 3.7903(10)|
| Pd1-Pd1#-Cl1#      | 108.51(5)|
| Pd1-Pd1#-Cl2#      | 91.59(5)|
| Pd1-Pd1#-S4#       | 87.95(5)|
| Pd1-Pd1#-S7#       | 72.80(4)|
| Pd1-S7#-Pd1#       | 72.61(4)|

# = −x, 2−y, −z
**Figure A2.** View of the herringbone packing of [PdCl$_2$([9]aneS$_2$O)] dimers in α-1 viewed along the $a$ (left) and $b$ (right) axes. Intermolecular Pd···Pd vectors are highlighted using a dashed bond, hydrogen atoms are omitted for clarity and displacement ellipsoids are shown at 50% probability.

**Structure of β-1**

Crystals of β-1 were originally obtained as orange blocks by diffusion of Et$_2$O vapor into a saturated solution of 1 in MeNO$_2$ at room temperature and were observed alongside crystals of α-1. All subsequent attempts to obtain β-1 by means of standard recrystallization methods proved unsuccessful.

The complex crystallizes in monoclinic space group $P2_1/c$ with $a = 9.3384(3)$, $b = 12.6575(4)$, $c = 9.0498(3)$ Å, $\beta = 92.260(3)^\circ$ and $V = 1068.87(6)$ Å$^3$. The palladium center is bound in a cis-Cl$_2$S$_2$ square planar coordination environment (Fig. A3; Table A6). The macrocyclic conformation features an exodentate oxygen atom [Pd···O = 3.404(3) Å] and therefore has no significant apical Pd···O interaction. The ligand conformation is assigned as [36] following Dale
analysis with corners at C3 and C6 (Table A6), but if a less strict definition of gauche angles is allowed this tends towards a [234] conformation with an additional pseudo corner at C8. The equatorial plane is distorted by out-of-plane bending of S7–Pd1–Cl1 [174.81(5)°] resulting in the metal locating slightly out the plane [0.0328(7) Å] in the direction away from the oxygen. However, when considering the ideal plane formed by S4, S7 and Cl2, the metal center is found to locate 0.0197(10) Å out of the plane towards the oxygen. Similarly to α-1, the molecules pack into dimeric units related by inversion centers, in this case with the Pd centers locating much more centrally over each other (Table A7). The perpendicular separation between their PdCl$_2$S$_2$ least-squares planes is 3.5237(10) Å. In contrast to α-1, the dimers pack into sheets in the $bc$ plane affording alternating hydrophilic and hydrophobic layers (Fig. A4).

Figure A3. View showing the experimentally determined structure of [PdCl$_2$([9]aneS$_2$O)] in β-1. Displacement ellipsoids are drawn at 50 % probability.
Table A6. Coordination environment and macrocycle conformation for β-1

| Bond Length /Å | Bond Angle /° | Torsion Angle/° |
|----------------|--------------|-----------------|
| Pd1-Cl1        | 2.3124(12)   | Cl1-Pd1-Cl2     | 94.27(4)         | O1-C2-C3-S4 | −58.0(4) |
| Pd1-Cl2        | 2.3214(11)   | Cl2-Pd1-S7      | 88.78(4)         | C2-C3-S4-C5 | 79.5(4)  |
| Pd1-S4         | 2.2699(11)   | S7-Pd1-S4       | 90.08(4)         | C3-S4-C5-C6 | −133.8(4) |
| Pd1-S7         | 2.2601(12)   | S4-Pd1-Cl1      | 86.94(4)         | S4-C5-C6-S7 | 45.4(5)  |
| Pd1···O1       | 3.404(3)     | Cl1-Pd1-S7      | 174.81(5)        | C5-C6-S7-C8 | 70.3(4)  |
|                |              | Cl2-Pd1-S4      | 178.50(5)        | C6-S7-C8-C9 | −95.3(4) |
|                |              |                  |                  | S7-C8-C9-O1 | 65.2(4)  |
|                |              |                  |                  | C8-C9-O1-C2 | −131.3(4) |
|                |              |                  |                  | C9-O1-C2-C3 | 135.5(4) |

Table A7. Inter-dimer geometry for α-1

| Atomic Distance /Å | Angle /° |
|--------------------|----------|
| Pd1-Cl1#           | 4.4577(14) | Pd1-Pd1#-Cl1# | 98.22(4) |
| Pd1-Cl2#           | 4.0822(13) | Pd1-Pd1#-Cl2# | 86.69(3) |
| Pd1-S4#            | 4.2415(13) | Pd1-Pd1#-S4#  | 92.26(3) |
| Pd1-S7#            | 4.0319(13) | Pd1-Pd1#-S7#  | 86.14(4) |
| Pd1-Pd1#           | 3.4946(7)  |               |          |

# = −x,1−y,−z
Figure A4. View of the layered packing of [PdCl$_2$([9]aneS$_2$O)] dimers in β-1. Intermolecular Pd···Pd vectors are highlighted using dashed bonds, hydrogen atoms are omitted for clarity and displacement ellipsoids are shown at 50% probability.

**Structure of γ-1**

Crystals of γ-1 were obtained as orange blocks by diffusion of Et$_2$O vapor into a solution of 1 in MeNO$_2$ at 30 and 35 °C.

The complex crystallizes in monoclinic space group $P2_1/n$ with $a = 7.02123(16)$, $b = 11.4020(3)$, $c = 13.3817(3)$ Å, $β = 96.785(2)^\circ$ and $V = 1063.78(5)$ Å$^3$. The palladium center is bound in a cis-Cl$_2$S$_2$ square planar coordination environment (Fig. A5; Table A8). The oxygen donor atom is exodentate [Pd···O = 3.378(3) Å] with the result that there is no significant intramolecular apical Pd···O interaction. The ligand conformation is assigned as [36] following Dale analysis with corners at C5 and C8 (Table A8), but if a less strict definition of gauche angles is allowed this tends towards a [234] conformation with an additional pseudo corner at
C2. The metal resides slightly out of the equatorial plane [0.0243(8) Å] in the opposite direction from the oxygen donor atom. Uniquely to the series, the molecules do not pack as dimers but are arranged such that the O donor of the macrocycle is directed towards the base of a neighboring molecule [Pd⋯O$_{i}$ = 3.212(3) Å; symmetry code i: 0.5−x, −0.5+y, 1.5−z] giving rise to chains that run parallel to the b axis (Fig. A6) and can be designated as C(5) following graph set analysis$^{7}$. This interaction lies somewhat outside the sum of the van der Waals radii [3.15 Å]$^{6}$ and so is not considered to represent a significant interaction.

![Figure A5](image)

**Figure A5.** View showing experimentally determined structure of [PdCl$_2$([9]aneS$_2$O)] in γ-1. Displacement ellipsoids are drawn at 50 % probability.
Table A8. Coordination environment and macrocycle conformation for γ-1

| Bond Length /Å | Bond Angle /° | Torsion Angle/° |
|----------------|---------------|-----------------|
| Pd1-Cl1        | 2.3079(12)    | Cl1-Pd1-Cl2     | 94.08(5)          |
| Pd1-Cl2        | 2.3245(12)    | Cl2-Pd1-S7      | 87.29(4)          |
| Pd1-S4         | 2.2575(13)    | S7-Pd1-S4       | 89.94(4)          |
| Pd1-S7         | 2.2665(12)    | S4-Pd1-Cl1      | 88.67(5)          |
| Pd1···O1#      | 3.212(3)      | Cl1-Pd1-S7      | 177.94(5)         |
|                |               | Cl2-Pd1-S4      | 177.10(5)         |
|                |               | S7-C8-O1        | 177.94(5)         |
|                |               | Cl2-Pd1-S4      | 177.10(5)         |
|                |               | C6-S7-C8-C9     | 135.4(4)          |
|                |               | S7-C8-C9-O1     | 135.4(4)          |
|                |               | C8-C9-O1-C2     | 177.94(5)         |
|                |               | C9-O1-C2-C3     | 133.4(4)          |

# = 0.5−x,−0.5+y,1.5−z

Figure A6. View of chain formation in the structure of [PdCl₂(9]aneS₂O)] in γ-1. Intermolecular Pd···O interaction are highlighted using a dashed bond, hydrogen atoms are omitted for clarity and displacement ellipsoids shown at 50 % probability.
**Structure of α-2**

Crystals of α-2 were readily obtained as pale green blocks by diffusion of Et₂O vapor into solutions of 2 in MeNO₂ at room temperature. They were also often found in recrystallizations carried out at 30 or 35 °C.

α-[PtCl₂([9]aneS₂O)] is isomorphous and isostructural with α-[PdCl₂([9]aneS₂O)]. The complex crystallizes in monoclinic space group *P*₂₁/n with *a* = 8.4525(2), *b* = 12.2690(2), *c* = 10.3536(2) Å, β = 105.542(2)° and *V* = 1034.5(5) Å³. The platinum center is bound in a [4+1] square based pyramidal coordination environment comprising a *cis*-Cl₂S₂ equatorial plane, with an apical O donor [Pt···O = 3.077(4) Å] lying within the sum of the relevant van der Waals radii [3.27 Å]. The macrocycle therefore adopts a facially-bound, *endodentate* conformation with respect to the oxygen donor and the conformation is assigned as [234] following Dale analysis with corners at C3, C6 and C8 (Fig. A7; Table A9). The metal is located slightly out of the equatorial plane [0.0094(8) Å] in the direction away from the apical oxygen. The molecules pack into dimeric units about an inversion center such that the Pt of one molecule lies approximately centrally over the Pt1−S7 bond of another (Table A10), with a perpendicular separation of 3.68151(12) Å between their PtCl₂S₂ least-squares planes. These dimers can then be considered as packing in ABAB alternating sheets in the *bc* plane generating a herringbone-like pattern when viewed along the *a* axis in the manner seen for α-1.
Figure A7. View of the experimentally determined structure of [PtCl$_2$([9]aneS$_2$O)] in α-2. Displacement ellipsoids are shown at 50 % probability.

Table A9. Coordination environment and macrocycle conformation for α-2

| Bond Length /Å | Bond Angle /° | Torsion Angle/° |
|----------------|---------------|-----------------|
| Pt1-C11        | 2.330(2)      | C11-Pt1-C12     | 91.60(6) O1-C2-C3-S4 | 48.0(7) |
| Pt1-C12        | 2.328(2)      | Cl2-Pt1-S7      | 89.36(6) C2-C3-S4-C5 | 41.7(5) |
| Pt1-S4         | 2.246(2)      | S7-Pt1-S4       | 90.57(6) C3-S4-C5-C6 | −124.1(5) |
| Pt1-S7         | 2.241(2)      | S4-Pt1-C11      | 88.47(6) S4-C5-C6-S7 | 29.7(7) |
| Pt1⋯O1         | 3.077(4)      | Cl1-Pt1-S7      | 178.75(6) C5-C6-S7-C8 | 82.5(5) |
| Cl2-Pt1-S4     | 179.84(6)     | C6-S7-C8-C9     | −49.8(6) S7-C8-C9-O1 | −54.9(7) |
|                |               | S7-C8-C9-O1     | −54.9(7) C8-C9-O1-C2 | 141.5(5) |
|                |               | C9-O1-C2-C3     | −128.0(6) C9-O1-C2-C3 | −128.0(6) |
Table A10. Inter-dimer geometry for α-2

| Atomic Distance /Å | Angle /°  |
|-------------------|-----------|
| Pt1-Cl1#          | 5.022(2)  | Pt1-Pt1#-Cl1#  |
| Pt1-Cl2#          | 4.497(2)  | Pt1-Pt1#-Cl2#  |
| Pt1-S4#           | 4.418(2)  | Pt1-Pt1#-S4#   |
| Pt1-S7#           | 3.860(2)  | Pt1-Pt1#-S7#   |
| Pt1-Pt1#          | 3.8237(4)| Pt1-S7#-Pt1#   |

# = −x, 2−y,−z

Structure of β-2

Crystals of β-2 were originally obtained as orange blocks by diffusion of Et₂O vapor into saturated solutions of 2 in MeNO₂ at 30 and 35 °C.

β-[PtCl₂([9]aneS₂O)] is isomorphous and isostructural with β-[PdCl₂([9]aneS₂O)]. The complex crystallizes in monoclinic space group P2₁/c with \(a = 9.4167(2)\), \(b = 12.6646(2)\), \(c = 9.0376(2)\) Å, \(β = 91.5300(2)^°\) and \(V = 1077.43(3)\) Å³. The platinum center is bound in a square planar cis-Cl₂S₂ coordination environment (Fig. A8; Table A11). The macrocycle adopts an equatorially bound, exodentate conformation with respect to the oxygen [Pt···O = 3.450(2) Å] and consequently does not display an apical Pt···O interaction. The ligand conformation is assigned as [36] following Dale analysis with corners at C3 and C6 (Table A11), but if a less strict definition of gauche angles is allowed this tends towards a [234] conformation with an additional pseudo corner at C8. The equatorial plane is distorted by out-of-plane bending of S7–Pt1–Cl1 [175.71(3)°] resulting in the metal locating slightly out the plane [0.0235(4) Å] in the direction away from the oxygen. In β-1, molecules pack into dimeric units over an inversion center with the Pt centers locating near centrally over one-another (Table A12) and a
perpendicular separation of 3.5471(6) Å between their PtCl$_2$S$_2$ least-squares planes. The dimers then pack into sheets in the $bc$ plane affording alternating hydrophilic and hydrophobic layers in the manner seen for $\beta$-2.

**Figure A8.** View of experimentally determined structure of [PtCl$_2$([9]aneS$_2$O)] in $\beta$-2. Displacement ellipsoids are drawn at 50 % probability.
Table A11. Coordination environment and macrocycle conformation for β-2

| Bond Length /Å | Bond Angle /° | Torsion Angle/° |
|----------------|---------------|-----------------|
| Pt1-Cl1        | 2.3221(8)     | Cl1-Pt1-Cl2     | 92.75(3)           | O1-C2-C3-S4 | -57.4(3)           |
| Pt1-Cl2        | 2.3266(8)     | Cl2-Pt1-S7      | 89.61(3)           | C2-C3-S4-C5 | 78.9(2)            |
| Pt1-S4         | 2.2542(7)     | S7-Pt1-S4       | 90.29(3)           | C3-S4-C5-C6 | -133.2(2)          |
| Pt1-S7         | 2.2494(7)     | S4-Pt1-Cl1      | 87.43(3)           | S4-C5-C6-S7 | 43.3(3)            |
| Pt1···O1       | 3.450(2)      | Cl1-Pt1-S7      | 175.71(3)          | C5-C6-S7-C8 | 72.3(2)            |
|                |               | Cl2-Pt1-S4      | 178.74(3)          | C6-S7-C8-C9 | -95.4(3)           |
|                |               |                  |                   | S7-C8-C9-O1 | 64.7(3)            |
|                |               |                  |                   | C8-C9-O1-C2 | -131.2(3)          |
|                |               |                  |                   | C9-O1-C2-C3 | 135.4(3)           |

Table A12. Inter-dimer geometry for α-2

| Atomic Distance /Å | Angle /° |
|--------------------|----------|
| Pt1-Cl1#           | 4.4569(9)| Pt1-Pt1#-Cl1# | 97.06(2) |
| Pt1-Cl2#           | 4.0974(9)| Pt1-Pt1#-Cl2# | 86.23(2) |
| Pt1-S4#            | 4.2702(8)| Pt1-Pt1#-S4#  | 92.51(2) |
| Pt1-S7#            | 4.0736(8)| Pt1-Pt1#-S7#  | 86.67(2) |
| Pt1-Pt1#           | 3.5294(2)|               |           |

#=−x,1−y,−z
References

1. CrysAlisPro, Agilent Technologies Ltd, Yarnton, England, UK.

2. Sheldrick, G. M. *Acta Crystallogr., Sect. A*. 2008, 64, 112–122.

3. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* 2009, 42, 339–341.

4. Lucas, C. R.; Liang, W.; Miller, D. O.; Bridson, J. N. *Inorg. Chem.* 1997, 36, 4508–4513.

5. Dale, J. *Acta Chem. Scand.* 1973, 27, 1115–1129.

6. Bondi, A. *J. Phys. Chem.* 1964, 68, 441–451.

7. Bernstein, J.; Davis, R. E.; Shimoni, R.; Chang, N.-L. *Angew. Chem. Int. Ed. Engl.* 1995, 34, 1555-1573.