Supplementary Information.

Unequivocal Experimental Evidence of the Relationship between Emission Energies and Aurophilic Interactions.

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1. Crystallographic study.

Three different crystals of the E-isomer of \([Au(C_6Cl_5)_2Ag([9]aneS_3)]_2\), of similar shape and size (see Methods section), were used in the acquisition of high-pressure diffraction data. The crystals continued to yield good-quality data well beyond the expected hydrostatic limit of 100 kbar for the pressure-transmitting medium used (4:1 MeOH/EtOH). The experiment was only terminated upon the clear onset of crystal degradation at a pressure of 149.4 kbar.

1.1. Variable temperature experiment.

The effects of temperature on the E-isomer of stoichiometry \([Au(C_6Cl_5)_2Ag([9]aneS_3)]_2\) were investigated by means of variable-temperature experiment. We determined the unit cell parameters at different temperatures with a ramp rate of 360 K/h between fixed temperatures (see Experimental Section and Table S1). When the temperature of the crystal was decreased from 298 to 130 K using a ramp rate of 360 K/h, a reversible phase transition from \(\beta\)-E to the original phase \(\alpha\)-E occurred between 250 and 200 K.

\[\text{Table S1. Unit cell parameters for phases } \alpha\text{-E and } \beta\text{-E obtained from the variable temperature experiments (first and second rows) and from the high-pressure experiments (third and fourth rows).}\]

| Phase | Pressure (kbar) | T (K) | Space Group | \(a(\text{Å})\) | \(b(\text{Å})\) | \(c(\text{Å})\) | \(\beta(\degree)\) | \(V(\text{Å}^3)\) |
|-------|----------------|-------|-------------|-------------|-------------|-------------|-------------|-------------|
| \(\alpha\text{-E}\) | 0 | 100 | C\(2/c\) | 23.4283(5) | 8.78750(10) | 28.331(6) | 111.604(2) | 5423.34(19) |
| \(\beta\text{-E}\) | 0 | 298 | P-1 | 8.8149(2) | 12.6499(3) | 26.538(5) | 84.040(6) | 2774.1(5) |
| \(\beta\text{-E}\) | 3.6 | 298 | P-1 | 8.7896(3) | 12.6265(4) | 26.530(5) | 83.985(7) | 2759.4(5) |
| \(\alpha\text{-E}\) | 6.2 | 298 | C\(2/c\) | 23.3544(15) | 8.54750(13) | 28.023(7) | 110.795(16) | 5229.6(14) |
Fig. S1. Calculated powder pattern for $\alpha$-E phase.

Fig. S2. Calculated powder pattern for $\beta$-E phase.
Table S2. Unit cell parameters taken from variable temperature experiment with a ramp rate of 360 K/h for E-[Au(C₆Cl₅)₂Ag([9]aneS₃)]₂ (α-E and β-E).

| T (K) | Space Group | a (Å)     | b (Å)     | c (Å)     | α (°)    | β (°)    | γ (°)    | V (Å³)  |
|-------|-------------|-----------|-----------|-----------|----------|----------|----------|---------|
| 298   | P-1         | 8.832(3)  | 12.674(5) | 26.592(8) | 83.11(3) | 84.08(3) | 71.16(3) | 2790(2) |
| 250   | P-1         | 8.819(3)  | 12.619(5) | 26.574(9) | 82.98(3) | 84.25(3) | 71.24(3) | 2773(2) |
| 200   | C2/c        | 23.630(11)| 8.772(4)  | 28.383(11)| 89.93(3) | 111.49(4)| 89.88(3) | 5474(4) |
| 150   | C2/c        | 23.503(8) | 8.781(3)  | 28.372(9) | 89.92(3) | 111.53(3)| 89.95(3) | 5446(3) |
| 130   | C2/c        | 23.492(14)| 8.751(5)  | 28.345(16)| 89.91(4) | 111.54(5)| 89.78(5) | 5420(5) |

1.2. Effects of pressure on the unit cell parameters.

Increasing pressure from ambient to 3.6 kbar results in small decreases, of 0.3, 0.2 and 0.004%, in the a, b and c unit cell dimensions, respectively. Subsequently, between 3.6 and 6.2 kbar, an exchange is observed in the a and b unit cell dimensions, accompanied by a change in the c unit cell dimension and a volume increase, indicative of a phase transition where the space group changes from P-1 to C2/c (see Table S1). Between 6.2 and 149.4 kbar, the unit cell dimensions a, b and c decrease by 14.4, 10.4 and 8.7%, respectively, while the β angle narrows from 110.795(16) to 108.21(18)° and the unit cell volume contracts by 28.9% (see Figs. S5–S6 and Table S3). This degree of volume contraction is comparable to those seen in previous high-pressure studies of gold(I) complexes.

Fig. S3. Molecular overlay of α-E-[Au(C₆Cl₅)₂Ag([9]aneS₃)]₂ (red) and β-E-[Au(C₆Cl₅)₂Ag([9]aneS₃)]₂ (black).
**Fig. S4.** Calculated powder pattern for $\alpha$-E-[Au(C$_6$Cl$_5$)$_2$Ag([9]aneS$_3$)]$_2$ at 6.24 kbar.

**Fig. S5.** Pressure dependence of the unit-cell $a$, $b$ and $c$ dimensions for E-[Au(C$_6$Cl$_5$)$_2$Ag([9]aneS$_3$)]$_2$. Note the crossover at around 5 kbar, which was confirmed by refinement of the structures.
Fig. S6. Pressure dependence of the unit-cell $\alpha$, $\beta$ and $\gamma$ dimension for $E$-[Au(C$_6$Cl$_3$)$_2$Ag([9]aneS$_3$)]. Note the crossover at around 5 kbar, which was confirmed by refinement of the structures.

Fig. S7. Pressure dependence of the unit-cell volume for $E$-[Au(C$_6$Cl$_3$)$_2$Ag([9]aneS$_3$)]. Note the crossover at around 5 kbar, which was confirmed by refinement of the structures.
Table S3. Unit cell parameters for the $E$-[Au(C₆Cl₅)₂Ag([9]aneS₃)]₂ between ambient pressure and 149.4 kbar.

| Pressure (kbar) | Pressure error (kbar) | Space Group | a (Å)       | b (Å)       | c (Å)       | α (°)      | β (°)      | γ (°)      | V (Å³)     |
|----------------|-----------------------|-------------|-------------|-------------|-------------|------------|------------|------------|------------|
| Compression    |                       |             |             |             |             |            |            |            |            |
| 0              | 0.5                   | P-1         | 8.8149 (2)  | 12.6499 (3) | 26.538 (5)  | 83.184 (5) | 84.040 (6) | 71.160 (2) | 2774.1 (5) |
| 0              | 0.5                   | P-1         | 8.8124 (3)  | 12.6570 (4) | 26.552 (4)  | 83.167 (7) | 84.070 (7) | 71.136 (3) | 2776.0 (4) |
| 0              | 0.5                   | P-1         | 8.8160 (3)  | 12.6485 (3) | 26.531 (5)  | 83.193 (6) | 84.021 (6) | 71.160 (3) | 2773.4 (5) |
| 3.65           | 2.0                   | P-1         | 8.7896 (3)  | 12.6265 (4) | 26.530 (5)  | 83.148 (7) | 83.985 (7) | 71.132 (3) | 2759.4 (5) |
| 6.24           | 1.0                   | C2/c        | 23.3544 (15)| 8.54750 (13)| 28.023 (7)  | 90         | 110.795 (16)| 90         | 5229.6 (15)|
| 9.03           | 0.7                   | C2/c        | 23.265 (3)  | 8.4889 (2)  | 27.817 (13) | 90         | 110.48 (3) | 90         | 5146 (3)   |
| 11.9           | 0.5                   | C2/c        | 23.0343 (17)| 8.38562 (19)| 27.674 (9)  | 90         | 110.01 (2) | 90         | 5022.7 (18)|
| 13.5           | 1.5                   | C2/c        | 22.996 (4)  | 8.3808 (4)  | 27.565 (19) | 90         | 109.88 (4) | 90         | 4996 (4)   |
| 21.3           | 1.5                   | C2/c        | 22.6342 (18)| 8.1465 (2)  | 27.489 (9)  | 90         | 109.71 (2) | 90         | 4771.7 (17)|
| 25.3           | 1.4                   | C2/c        | 22.5307(8)  | 8.1113(2)   | 27.456 (19) | 90         | 109.717 (7)| 90         | 4723.5(8)  |
| 34.3           | 1.0                   | C2/c        | 22.1408 (17)| 8.00587 (18)| 27.327 (9)  | 90         | 109.65 (2) | 90         | 4561.8 (16)|
| 41.2           | 1.1                   | C2/c        | 21.847 (10) | 7.9419 (8)  | 27.48 (5)   | 90         | 109.36 (12)| 90         | 4498 (9)   |
| 48.7           | 0.6                   | C2/c        | 21.7321 (19)| 7.9142 (2)  | 27.073 (10) | 90         | 109.52 (2) | 90         | 4388.7 (18)|
| 53.7           | 3.6                   | C2/c        | 21.442 (5)  | 7.8469 (4)  | 26.97 (3)   | 90         | 109.32 (6) | 90         | 4282.5 (5) |
| 58.6           | 1.2                   | C2/c        | 21.222 (3)  | 7.8628 (3)  | 26.913 (14) | 90         | 109.29 (3) | 90         | 4279 (2)   |
| 66.9           | 1.1                   | C2/c        | 21.220 (3)  | 7.8301 (4)  | 26.741 (16) | 90         | 108.99 (4) | 90         | 4201 (3)   |
| 74.8           | 3.2                   | C2/c        | 21.089 (3)  | 7.7928 (3)  | 26.668 (15) | 90         | 108.98 (3) | 90         | 4144 (3)   |
| 100.3          | 3.1                   | C2/c        | 20.617 (5)  | 7.7051 (6)  | 26.32 (3)   | 90         | 108.30 (7) | 90         | 3970 (5)   |
| 129.1          | 1.9                   | C2/c        | 20.323(5)   | 7.6796(5)   | 25.76(3)    | 90         | 108.22(6)  | 90         | 3819(5)    |
| 149.4          | 0.7                   | C2/c        | 19.980(15)  | 7.6558(14)  | 25.58(8)    | 90         | 108.21(18) | 90         | 3717(13)   |
| Decompression  |                       |             |             |             |             |            |            |            |            |
| 96.4           | 0.8                   | C2/c        | 20.473(11)  | 7.7638(8)   | 26.41(6)    | 90         | 108.22(13) | 90         | 3987(9)    |
| 24.7           | 3.2                   | C2/c        | 22.549(6)   | 8.1533(5)   | 27.46(3)    | 90         | 109.78(6)  | 90         | 4751(6)    |
| 14.3           | 0.7                   | C2/c        | 23.003(5)   | 8.3280(4)   | 27.64(2)    | 90         | 110.03(5)  | 90         | 4975(4)    |
| 10             | 0.7                   | C2/c        | 23.212(5)   | 8.4325(5)   | 27.77(2)    | 90         | 110.12(6)  | 90         | 5104(4)    |
| 5.25           | 0.8                   | P-1         | 8.6157(16)  | 12.541(3)   | 26.548(7)   | 90.73(2)   | 99.12(2)   | 110.059(19)| 2653.5(11)|
## 1.3. Effects of pressure on the molecular geometry.

Table S4. Selected experimental structural parameters for $E$-[Au(C$_6$Cl$_3$)$_2$Ag([9]aneS$_3$)$_2$] between ambient pressure and 149.4 kbar.

| Pressure (kbar) | Au···Au (Å) | π-π A (Å) | π-π B (Å) | Disorder π-π A (Å) | Disorder π-π B (Å) | Ag$_{1A}$···Cl$_6$ (Å) | Ag$_{1A}$-Cl$_{26}$ (Å) | Ag$_{1A}$-Au-Au (°) | Ag$_{1A}$-Ag$_{1A}$ (Å) |
|----------------|-------------|-----------|-----------|-------------------|-------------------|-----------------------|-----------------------|-------------------|----------------------|
| Compression    |             |           |           |                   |                   |                       |                       |                   |                      |
| 0              | 3.3955(9)   | 3.642     | 3.606     | --                | --                | 3.762(5)              | --                    | 140.00(8)         | 7.990(3)           |
| 0              | 3.3962(7)   | 3.635     | 3.612     | --                | --                | 3.405(4)              | --                    | 139.60(5)         | 7.995(2)           |
| 0              | 3.3938(9)   | 3.639     | 3.601     | --                | --                | 3.402(6)              | --                    | 139.60(8)         | 7.995(3)           |
| 3.65           | 3.3767(11)  | 3.629     | 3.601     | --                | --                | 3.388(7)              | --                    | 139.67(10)        | 7.982(4)           |
| 6.24           | 3.274(2)    | 3.535     | 3.535     | --                | --                | 3.394(3)              | --                    | 139.57(6)         | 7.866(3)           |
| 9.03           | 3.233(3)    | 3.513     | 3.513     | --                | --                | 3.376(5)              | --                    | 140.19(9)         | 7.841(5)           |
| 11.9           | 3.173(3)    | 3.528     | 3.528     | --                | --                | 3.306(10)             | --                    | 140.99(9)         | 7.811(1)           |
| 13.5           | 3.160(6)    | 3.440     | 3.440     | --                | --                | 3.312(10)             | --                    | 141.31(16)        | 7.806(9)           |
| 21.3           | 3.115(4)    | --        | --        | 3.265             | 3.729             | 2.65(2)               | 3.121(16)             | 133.63(18)        | 148.38(15)         | 7.22(2)            |
| 25.3           | 3.098(5)    | --        | --        | 3.240             | 3.721             | 2.61(2)               | 3.068(18)             | 132.96(18)        | 148.68(17)         | 7.15(3)            |
| 34.3           | 3.0300(15)  | --        | --        | 3.118             | 3.619             | 2.545(6)              | 3.115(8)              | 131.03(6)         | 149.76(7)          | 6.866(18)          |
| 41.2           | 2.987(3)    | --        | --        | 3.142             | 3.649             | 2.485(8)              | 3.025(12)             | 129.82(11)        | 150.04(12)         | 6.716(6)           |
| 48.7           | 2.962(2)    | --        | --        | 3.094             | 3.624             | 2.443(6)              | 3.004(9)              | 129.08(7)         | 150.87(8)          | 6.595(17)          |
| 53.7           | 2.924(3)    | --        | --        | 3.009             | 3.569             | 2.43(3)               | 2.98(3)               | 127.64(15)        | 151.13(3)          | 6.436(6)           |
| 58.6           | 2.926(2)    | --        | --        | 3.080             | 3.660             | 2.355(10)             | 2.912(8)              | 127.17(7)         | 150.61(8)          | 6.413(8)           |
| 66.9           | 2.908(3)    | --        | --        | 2.998             | 3.589             | 2.337(8)              | 2.890(11)             | 125.73(10)        | 149.91(12)         | 6.264(12)          |
| 74.8           | 2.881(3)    | --        | --        | 3.025             | 3.618             | 2.282(8)              | 2.832(10)             | 125.33(10)        | 150.51(12)         | 6.202(12)          |
| 100.3          | 2.828(4)    | --        | --        | 3.007             | 3.680             | 2.21(4)               | 2.70(3)               | 122.5(4)          | 149.3(3)           | 5.97(6)            |
| 129.1          | 2.827(5)    | --        | --        | 2.957             | 3.630             | 2.182(15)             | 2.521(18)             | 118.0(3)          | 149.0(3)           | 5.44(5)            |
| 149.4          | 2.758(11)   | --        | --        | 2.548             | --                | 1.983(17)             | 2.17(2)               | 111.6(4)          | 153.1(4)           | 4.74(4)            |
| Decompression  |             |           |           |                   |                   |                       |                       |                   |                      |
| 96.4           | 2.847(12)   | --        | --        | 2.835             | --                | 2.05(4)               | 2.59(5)               | 120.0(6)          | 148.3(6)           | 5.79(8)            |
| 24.7           | 3.096(8)    | 3.390     | 3.390     | --                | --                | 3.23(3)               | --                    | 141.7(2)          | --                   | 7.66(3)            |
| 14.3           | 3.171(7)    | 3.445     | 3.445     | --                | --                | 3.310(17)             | --                    | 141.44(16)        | --                   | 7.805(19)          |
| 10             | 3.217(8)    | 3.488     | 3.488     | --                | --                | 3.35(3)               | --                    | 141.0(2)          | --                   | 7.86(2)            |
| 5.25           | 3.321(5)    | 3.623     | 3.593     | --                | --                | 3.44(3)               | --                    | 140.8(4)          | --                   | 7.915(15)          |
Table S5. Selected experimental structural parameters for $E$-[Au(C₆Cl₅)₂Ag([9]aneS₃)]$_2$ between ambient pressure and 149.4 kbar.

| Pressure (kbar) | $Ag_{IA}-Ag_{IA}$ (Å) | $Au_{1}-Ag_{1}$ | $Au_{2}-Ag_{2}$ | $Au_{1}-Ag_{IA}$ | $Ag_{1}-C_{1}$ (Å) | $Ag_{1}-C_{21}$ (Å) | $Ag_{IA}-C_{1}$ (Å) | $Ag_{IA}-C_{21}$ (Å) | $C_{1}-Au_{1}-C_{7}$ (°) | $C_{21}-Au_{2}-C_{7}$ (°) |
|-----------------|------------------------|-----------------|-----------------|-----------------|------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Compression     |                        |                 |                 |                 |                  |                   |                   |                   |                   |                   |
| 0               | --                     | 2.722(3)        | 2.728(3)        | --              | 2.547(10)        | --                | --                | --                | 174.0(5)          | --                |
| 0               | --                     | 2.734(2)        | 2.722(2)        | --              | 2.499(8)         | --                | --                | --                | 175.5(4)          | --                |
| 0               | --                     | 2.731(3)        | 2.727(3)        | --              | 2.502813         | --                | --                | --                | 175.2(6)          | --                |
| 3.65            | --                     | 2.733(4)        | 2.726(4)        | --              | 2.509(14)        | --                | --                | --                | 175.2(6)          | --                |
| 6.24            | --                     | 2.7358(18)      | --              | --              | 2.505(14)        | --                | --                | --                | 171.7(4)          | --                |
| 9.03            | --                     | 2.734(3)        | --              | --              | 2.478(11)        | --                | --                | --                | 171.9(5)          | --                |
| 11.9            | --                     | 2.736(5)        | --              | --              | 2.424(13)        | --                | --                | --                | 171.4(6)          | --                |
| 13.5            | --                     | 2.737(5)        | --              | --              | 2.462(2)         | --                | --                | --                | 175.5(11)         | --                |
| 21.3            | 8.087(18)              | 2.767(12)       | --              | 2.729(10)       | 2.31(2)          | 2.75(3)           | 2.135(17)         | 2.60(3)           | 166.9(9)          | 170.0(8)          |
| 25.3            | 8.09(2)                | 2.773(14)       | --              | 2.733(14)       | 2.30(3)          | 2.77(3)           | 2.10(2)           | 2.59(3)           | 166.5(13)         | 169.3(10)         |
| 34.3            | 8.166(18)              | 2.755(4)        | --              | 2.762(4)        | 2.467(5)         | 2.831(8)          | 2.172(3)          | 2.634(9)          | 166.24(8)         | 170.71(13)        |
| 41.2            | 8.102(8)               | 2.756(6)        | --              | 2.769(7)        | 2.442(6)         | 2.819(9)          | 2.064(4)          | 2.559(11)         | 165.64(10)        | 172.80(14)        |
| 48.7            | 8.07(2)                | 2.746(4)        | --              | 2.754(4)        | 2.454(5)         | 2.857(8)          | 2.065(3)          | 2.576(9)          | 165.18(8)         | 170.92(13)        |
| 53.7            | 8.002(11)              | 2.753(10)       | --              | 2.734(11)       | 2.54(3)          | 2.89(4)           | 2.03(2)           | 2.56(4)           | 164.1(7)          | 171.6(10)         |
| 58.6            | 7.957(8)               | 2.761(4)        | --              | 2.715(4)        | 2.451(8)         | 2.870(12)         | 1.93(1)           | 2.490(16)         | 163.7(5)          | 171.9(5)          |
| 66.9            | 7.846(11)              | 2.763(6)        | --              | 2.675(6)        | 2.525(7)         | 2.945(8)          | 1.879(4)          | 2.479(10)         | 162.92(9)         | 173.49(14)        |
| 74.8            | 7.866(12)              | 2.761(6)        | --              | 2.689(6)        | 2.473(7)         | 2.912(8)          | 1.860(4)          | 2.452(10)         | 163.11(9)         | 171.38(14)        |
| 100.3           | 7.72(4)                | 2.796(19)       | --              | 2.65(2)         | 2.64(4)          | 2.92(3)           | 1.72(3)           | 2.37(4)           | 156.1(11)         | 172.9(14)         |
| 129.1           | 7.58(4)                | 2.725(13)       | --              | 2.568(18)       | 2.684(11)        | 2.864(13)         | 1.647(11)         | 2.245(18)         | 158.1(3)          | 174.4(2)          |
| 149.4           | 7.99(4)                | 2.662(12)       | --              | 2.77(2)         | 3.020(13)        | 3.050(16)         | 2.091(17)         | 2.75(3)           | 164.4(4)          | 167.5(7)          |
| Decompression   |                        |                 |                 |                 |                  |                   |                   |                   |                   |                   |
| 96.4            | 7.65(8)                | 2.82(3)         | --              | 2.61(4)         | 2.56(6)          | 3.13(7)           | 1.71(5)           | 2.50(7)           | 161.7(15)         | 171(3)            |
| 24.7            | --                     | 2.712(15)       | --              | --              | 2.47(4)          | --                | --                | --                | 172.0(18)         | --                |
| 14.3            | --                     | 2.735(10)       | --              | --              | 2.53(4)          | --                | --                | --                | 172.7(14)         | --                |
| 10              | --                     | 2.740(13)       | --              | --              | 2.49(7)          | --                | --                | --                | 174(3)            | --                |
| 5.25            | --                     | 2.703(13)       | 2.733(16)       | --              | 2.50(4)          | --                | --                | --                | 169(2)            | --                |
Table S6. Torsion angles from the macrocyclic ligand component defined by the donor atoms S1, S2 and S3.

| Pressure (kbar) | S1-C13-C14-S2 | C13-C14-S2-C15 | C14-S2-C15-C16 | S2-C15-C16-S3 | C15-C16-S3-C17 | C16-S3-C17-C18 | S3-C17-C18-S1 | C17-C18-S1-C13 | C18-S1-C13-C14 |
|----------------|---------------|----------------|----------------|---------------|----------------|----------------|---------------|----------------|----------------|
| 0              | 57(3)         | 128.7(18)      | 57(2)          | 128.8(15)     | 54.4(17)       | 58(2)          | 129(2)        | 55(2)          |
| 0              | 52(3)         | 125.9(18)      | 52.28(17)      | 124.6(17)     | 56(3)          | 47(3)          | 121.2(19)     | 72(2)          |
| 0              | 55(3)         | 127(2)         | 54(3)          | 124.3(3)      | 56(3)          | 48(4)          | 120(2)        | 67(3)          |
| 3.65           | 57(4)         | 128(3)         | 53(3)          | 127(3)        | 62(4)          | 41(5)          | 118(3)        | 68(3)          |
| 6.24           | 59(2)         | 128.6(12)      | 53.2(15)       | 130.7(19)     | 56.4(15)       | 54(2)          | 127(2)        | 57(3)          |
| 9.03           | 59(2)         | 129.3(15)      | 54.1(16)       | 130.3(18)     | 58(2)          | 53(3)          | 127(2)        | 57(2)          |
| 11.9           | 61(4)         | 128(3)         | 55(4)          | 129(4)        | 60(4)          | 49(4)          | 123(3)        | 56(4)          |
| 13.5           | 65(5)         | 133(3)         | 54(4)          | 132(4)        | 57(4)          | 51(6)          | 125(4)        | 56(4)          |
| 21.3           | 57(7)         | 133(5)         | 61(6)          | 130(11)       | 56(6)          | 48(7)          | 129(6)        | 60(7)          |
| 25.3           | 53(10)        | 133(6)         | 57(8)          | 134(10)       | 54(6)          | 49(8)          | 132(6)        | 64(8)          |
| 34.3           | 48(3)         | 118.2(17)      | 60.0(14)       | 132.1(14)     | 52.8(16)       | 48.7(16)       | 131.2(11)     | 65.9(12)       |
| 41.2           | 15(5)         | 99(4)          | 62.0(14)       | 137.9(14)     | 50(2)          | 55(2)          | 132.2(12)     | 82(3)          |
| 48.7           | 35(3)         | 116.9(18)      | 66.2(14)       | 142.3(15)     | 52.3(17)       | 46.4(18)       | 130.1(11)     | 69(2)          |
| 53.7           | 17(15)        | 100(10)        | 94(17)         | 12(25)        | 110(15)        | 71(6)          | 36(8)         | 126(7)         | 88(11)          |
| 58.6           | 39(3)         | 120.8(16)      | 68.6(14)       | 142.7(16)     | 55.9(17)       | 39.1(18)       | 124.1(11)     | 69(2)          |
| 66.9           | 47(3)         | 124.2(17)      | 58.5(15)       | 143.7(16)     | 53.0(18)       | 45.2(19)       | 128.4(12)     | 64(2)          |
| 74.8           | 44(3)         | 128.9(17)      | 67.7(15)       | 137.9(19)     | 52(2)          | 43(2)          | 129.5(12)     | 71(2)          |
| 100.3          | 59(11)        | 142(8)         | 48(10)         | 159(12)       | 54(7)          | 49(12)         | 151(13)       | 64(11)         |
| 129.1          | 83.8(11)      | 120.4(10)      | 7.7(11)        | 90.8(11)      | 148.6(8)       | 79.0(12)       | 22.1(13)      | 119.4(10)      | 62.4(10)        |
| 149.4          | 59.1(14)      | 145.6(11)      | 20.0(15)       | 64.8(16)      | 113.9(12)      | 137.5(12)      | 71.7(16)      | 46.7(14)       | 71.1(13)        |

| Decompression  | 76(3)         | 126(5)         | 5(7)           | 81(6)         | 134(4)         | 122(6)         | 32(8)         | 78(7)          | 75(5)          |
| 24.7           | 62(7)         | 132(4)         | 59(5)          | 56(7)         | 130(5)         | 63(6)          | 51(8)         | 125(7)         | 51(7)          |
| 14.3           | 58(4)         | 130(3)         | 53(3)          | 61(4)         | 130(3)         | 53(4)          | 56(5)         | 128(4)         | 58(4)          |
| 10             | 55(6)         | 127(4)         | 56(5)          | 127(5)        | 52(5)          | 60(7)          | 129(6)        | 60(6)          |
| 5.25           | 31(9)         | 110(11)        | 74(9)          | 36(10)        | 129(9)         | 64(5)          | 65(11)        | 125(8)         | 49(8)          |
Table S7. Torsion angles from the macrocyclic ligand component defined by the donor atoms S1A, S2A and S3A.

| Pressure (kbar) | S1-C13-C14-S2 | C13-C14-S2-C15 | C14-S2-C15-C16 | S2-C15-C16-S3 | C15-C16-S3-C17 | C16-S3-C17-C18 | S3-C17-C18-S1 | C17-C18-S1-C13 | C18-S1-C13-C14 |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0              | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 0              | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 0              | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 3.65           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 6.24           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 9.03           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 11.9           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 13.5           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 21.3           | 49(8)          | 125(5)         | 48(6)          | 65(8)          | 134(6)         | 60(6)          | 56(8)          | 127(6)         | 65(8)          |
| 25.3           | 50(10)         | 129(6)         | 51(7)          | 56(9)          | 132(7)         | 63(7)          | 57(10)         | 132(8)         | 67(9)          |
| 34.3           | 39(3)          | 125(2)         | 47.4(14)       | 62.7(13)       | 133.8(119)     | 57(3)          | 61(3)          | 133.9(13)      | 74.9(15)       |
| 41.2           | 48(4)          | 127(4)         | 41.9(17)       | 70.2(14)       | 135.68(12)     | 52(3)          | 64(4)          | 128.6(14)      | 70.1(19)       |
| 48.7           | 52(3)          | 133(3)         | 48.5(18)       | 54.9(18)       | 128.2(12)      | 57(3)          | 67(3)          | 139.7(14)      | 69.1(16)       |
| 53.7           | 56(8)          | 134(6)         | 31(5)          | 88(5)          | 151(6)         | 48(9)          | 52(10)         | 128(7)         | 77(6)          |
| 58.6           | 51(4)          | 133(4)         | 45.5(19)       | 54.2(18)       | 130.2(12)      | 58(3)          | 66(3)          | 142.2(14)      | 72.5(17)       |
| 66.9           | 53(5)          | 135(5)         | 48(2)          | 57.6(17)       | 127.9(14)      | 58(5)          | 52(5)          | 126.1(18)      | 77.3(19)       |
| 74.8           | 55(4)          | 132(3)         | 48(2)          | 57.9(19)       | 130.9(13)      | 56(3)          | 66(3)          | 137.9(16)      | 68.0(19)       |
| 100.3          | 80(10)         | 125(9)         | 131(42)        | 35(45)         | 89(14)         | 180(11)        | 90(10)         | 50(10)         | 66(13)         |
| 129.1          | 79.4(12)       | 2.1(12)        | 136.2(9)       | 82.8(11)       | 62.2(11)       | 47.7(13)       | 66.7(13)       | 138.3(9)       | 116.2(11)      |
| 149.4          | 37.6(18)       | 49.7(17)       | 160.9(10)      | 55.4(15)       | 63.9(13)       | 44.7(14)       | 74.6(15)       | 150.1(9)       | 104.3(15)      |
| Compression    |                |                |                |                |                |                |                |                |                |
| 0              | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 24.7           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 14.3           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 10             | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 5.25           | --             | --             | --             | --             | --             | --             | --             | --             | --             |

Decompression

| Pressure (kbar) | S1-C13-C14-S2 | C13-C14-S2-C15 | C14-S2-C15-C16 | S2-C15-C16-S3 | C15-C16-S3-C17 | C16-S3-C17-C18 | S3-C17-C18-S1 | C17-C18-S1-C13 | C18-S1-C13-C14 |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 96.4           | 74(4)          | 1(5)           | 137(4)         | 90(5)          | 59(4)          | 53(6)          | 56(9)          | 142(4)         | 121(5)         |
| 24.7           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 14.3           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 10             | --             | --             | --             | --             | --             | --             | --             | --             | --             |
| 5.25           | --             | --             | --             | --             | --             | --             | --             | --             | --             |
1.3.1. Molecular disorder.

At pressures above 21.3 kbar, disorder affects almost the whole structure (see Fig. S8): the entire $[\text{Ag}([9]\text{aneS}_3)]^+$ cationic fragment is disordered, as are both of the pentachlorophenyl ligands. In order to allow the analysis of structural trends, it was necessary to identify which disorder components were mutually compatible since these decisions determine which of the derived distances and angles are chemically sensible and therefore valid.

![Molecular disorder](image)

**Fig. S8.** Molecular disorder of the $\alpha$-$E$-$[\text{Au}(\text{C}_6\text{Cl}_5)_2\text{Ag}([9]\text{aneS}_3)]_2$.

1.3.2. Conformation of the macrocycle.

The $[9]\text{aneS}_3$ macrocycle is endodentate and facially coordinating to the Ag centre in all phases. In the disorder component containing the atoms S1, S2 and S3, the conformation can be described in the Dale notation as [333] and this remains unchanged until 129.1 kbar. When the pressure is increased towards 149.4 kbar and subsequently decreased to 96.4 kbar, the conformation can be described as [234], before reverting to [333] as the pressure is lowered further (see Tables S5 and S6). The disorder component defined by S1A, S2A and S3A displays a [333] conformation up to a pressure of 74.8 kbar. At higher pressures the conformation is [234], reverting to [333] when the pressure is decreased to 96.4 kbar, as seen for the first disorder component.
1.3.3. \([\text{Ag([9]aneS}_3])^+\) fragment.

Upon increasing the pressure, the \([\text{Ag([9]aneS}_3])^+\) cation changes its position along the \(b\) axis direction such that the Ag centres move closer together. The molecular disorder affecting this cation involves one disorder component moving slightly from its position with increasing pressure, while the other shifts more significantly. We have identified two parameters, the Ag···Ag distance and the Ag···Au···Au angle, which allow us to quantify the change in the position of the \([\text{Ag([9]aneS}_3])^+\) cation. In one component the Ag···Ag distance ranges between 8.116 and 7.58 Å, while in the other component the Ag···Ag distance shortens to 4.74 Å (see Tables S4 and S5 and Fig. S9). As we can see in Figure S10, the Ag···Au···Au angle in one of disorder components remains at around 150° throughout, while in the other component it decreases linearly from 133° reaching a value of 111° at 149.4 kbar.

![Fig. S9. Pressure dependence of the Ag···Ag interaction angle for the \(E\)-\([\text{Au(C}_6\text{Cl}_3)_2\text{Ag([9]aneS}_3)]_2\).](image)
Fig. S10. Pressure dependence of the Ag···Au···Au interaction angle for the $E$-[Au(C$_6$Cl$_5$)$_2$Ag([9]aneS$_3$)$_2$].

Moreover, the shift of the [Ag([9]aneS$_3$)]$^+$ cation gives rise to a new contact between Ag1 and a Cl atom in an *ortho* position on a phenyl ring and to the breaking of an existing Ag···C$_{ipso}$ contact. Taking into account the disorder in the pentachlorophenyl ligands, we have measured all the possible distances involved in these contacts. Although the Ag1···Cl distance shows a linear trend, decreasing as a function of the pressure (*Table S3, Fig. S11*), no such trend is seen in the Ag···C$_{ipso}$ distance (*Table S4, Fig. S12*).

Fig. S11. Pressure dependence of the Ag···Cl interaction distance for the $E$-[Au(C$_6$Cl$_5$)$_2$Ag([9]aneS$_3$)$_2$].
1.3.4. \([\text{Au(C}_6\text{Cl}_5\text{)}^2\text{]}\) fragment.

We have identified parameters, namely the C1⋯Au⋯C7 and the C21⋯Au⋯C7 angles of the \(E\)-isomer, which allow us to monitor both the effects of pressure and the extent of the disorder within the \([\text{Au(C}_6\text{Cl}_5\text{)}^2\text{]}\) fragment. As the pressure increases, the C1⋯Au⋯C7 angle decreases from a value close to 180° to approximately 156°, clearly indicating a decrease in linearity. In contrast, the C21⋯Au⋯C7 angle shows little variation with pressure, remaining close to an average value of 171(2)°; see Table S4 and Fig. S13.
In order to investigate the changes in the π-π interactions as a function of pressure, we measured the centroid-centroid distances between the neighbouring pentachlorophenyl ligands. As noted previously, these ligands also exhibit disorder, so that the corresponding distances for each disorder component were measured (see Table S3 and Fig. S14). For one of the disorder components the distance decreases with increasing pressure, suggesting a stronger π···π interaction, while no clear trend is observed for the other component.
Fig. S14. Pressure dependence of the centroid-centroid distance in the $\pi \cdots \pi$ interaction for the $E$-$[\text{Au(C}_6\text{Cl}_5\text{)}_2\text{Ag([9]aneS}_3\text{)]}_2]$. 
Table S8. Crystallographic data for $E$-[Au(C₆Cl₅)]₂Ag([9]aneS₃)]₂ between ambient pressure and 149.4 kbar.

| Experiment number - Pressure | Exp. 2.1 - 0 kbar | Exp. 6.1 - 0 kbar | Exp. 7.1 - 0 kbar | Exp. 2.2 – 3.65 kbar | Exp. 7.2A – 6.24 kbar |
|------------------------------|-------------------|-------------------|-------------------|----------------------|----------------------|
| _chemical_formula_sum        | C₁₈H₁₂AgAuCl₁₀S₃ | C₁₈H₁₂AgAuCl₁₀S₃ | C₁₈H₁₂AgAuCl₁₀S₃ | C₁₈H₁₂AgAuCl₁₀S₃    | C₁₈H₁₂AgAuCl₁₀S₃    |
| _exptl_crystal_colour        | green             | green             | green             | green                | green                |
| _exptl_crystal_description   | prism             | prism             | prism             | prism                | prism                |
| _exptl_crystal_size_max      | 0.12              | 0.163             | 0.09              | 0.12                 | 0.09                 |
| _exptl_crystal_size_mid      | 0.06              | 0.117             | 0.08              | 0.06                 | 0.08                 |
| _exptl_crystal_size_min      | 0.03              | 0.061             | 0.013             | 0.03                 | 0.013                |
| _space_group_crystal_system  | triclinic         | triclinic         | triclinic         | triclinic            | monoclinic           |
| _space_group_name_H-M_alt    | P -1              | P -1              | P -1              | P -1                 | C 1 2/c 1            |
| _space_group_name_Hall       | -P 1              | -P 1              | -P 1              | -P 1                 | -C 2yc               |
| _cell_length_a               | 8.8149(2)         | 8.8124(3)         | 8.8160(3)         | 8.7896(3)            | 23.3544(15)          |
| _cell_length_b               | 12.6499(3)        | 12.6570(4)        | 12.6485(3)        | 12.6265(4)           | 8.54750(13)          |
| _cell_length_c               | 26.538(5)         | 26.552(4)         | 26.531(5)         | 26.530(5)            | 28.023(7)            |
| _cell_angle_alpha            | 83.184(5)         | 83.167(7)         | 83.193(6)         | 83.148(7)            | 90                   |
| _cell_angle_beta             | 84.040(6)         | 84.070(7)         | 84.021(6)         | 83.985(7)            | 110.795(16)          |
| _cell_angle_gamma            | 71.160(2)         | 71.136(3)         | 71.160(3)         | 71.132(3)            | 90                   |
| _cell_volume                 | 2774.1(5)         | 2776.0(4)         | 2773.4(5)         | 2759.4(5)            | 5229.6(14)           |
| _cell_formula_units_Z        | 4                 | 4                 | 4                 | 4                    | 8                    |
| _exptl_crystal_density_diffnm| 2.356             | 2.354             | 2.356             | 2.368                | 2.499                |
| _chemical_formula_weight     | 983.79            | 983.79            | 983.79            | 983.79               | 983.79               |
| _exptl_crystal_F_000         | 1856              | 1856              | 1856              | 1856                 | 3712                 |
| _diffrn_ambient_temperature | 293               | 293               | 293               | 293                  | 293                  |
| _cell_measurement_temperature| 293               | 293               | 293               | 293                  | 293                  |
| _diffrn_reflns_theta_max    | 27.693            | 27.854            | 27.941            | 27.789               | 27.873               |
| _exptl_absorpt_coefficient_mu| 7.188             | 7.183             | 7.190             | 7.226                | 7.626                |
| _diffrn_reflns_number       | 25699             | 27102             | 27086             | 24573               | 35064               |
| _cell_measurement_reflcs_used| 5540              | 7649              | 5724              | 5644                | 9563                 |
| _refine_ls_R_factor_gt      | 0.0522            | 0.0385            | 0.0486            | 0.0600               | 0.0348               |
| _refine_ls_wR_factor_ref     | 0.0972            | 0.0783            | 0.0987            | 0.1742               | 0.0781               |
| _refine_ls_number_parameters| 547               | 547               | 547               | 548                  | 298                  |
| _refine_ls_number_restraints| 982               | 910               | 678               | 931                  | 306                  |
| _refine_ls_goodness_of_fit_ref | 1.044         | 1.050             | 1.027             | 1.055                | 1.096                |
| Experiment number - Pressure | Exp. 6.2 – 9.03 kbar | Exp. 7.3 – 11.9 kbar | Exp. 6.3 – 13.5 kbar | Exp. 7.4 – 21.3 kbar | Exp. 2.3 – 25.3 kbar |
|-----------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| **chemical_formula_sum**    | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} |
| **exptl_crystal_colour**    | green                | green                | green                | yellowish green      | yellowish green      |
| **exptl_crystal_description** | prism               | prism               | prism               | prism               | prism               |
| **exptl_crystal_size_max**  | 0.163                | 0.09                 | 0.163                | 0.09                 | 0.12                |
| **exptl_crystal_size_mid** | 0.117                | 0.08                 | 0.117                | 0.08                 | 0.06                |
| **exptl_crystal_size_min** | 0.061                | 0.013                | 0.061                | 0.013                | 0.03                |
| **space_group_crystal_system** | monoclinic          | monoclinic          | monoclinic          | monoclinic          | monoclinic          |
| **space_group_name_H-M_alt** | C 1 2/c 1           | C 1 2/c 1           | C 1 2/c 1           | C 1 2/c 1           | C 1 2/c 1           |
| **space_group_name_Hall**   | -C 2yc              | -C 2yc              | -C 2yc              | -C 2yc              | -C 2yc              |
| **cell_length_a**           | 23.265(3)           | 23.0343(17)         | 22.996(4)           | 22.6342(18)         | 22.5307(8)          |
| **cell_length_b**           | 8.4889(2)           | 8.38562(19)         | 8.3808(4)           | 8.1465(2)           | 8.1113(2)           |
| **cell_length_c**           | 27.817(13)          | 27.674(9)           | 27.565(19)          | 27.489(9)           | 27.456(4)           |
| **cell_angle_alpha**        | 90                   | 90                   | 90                   | 90                   | 90                   |
| **cell_angle_beta**         | 110.48(3)           | 110.01(2)           | 109.88(4)           | 109.71(2)           | 109.717(7)          |
| **cell_angle_gamma**        | 90                   | 90                   | 90                   | 90                   | 90                   |
| **cell_volume**             | 5146(3)             | 5022.7(17)          | 4996(4)             | 4771.7(17)          | 4723.5(8)           |
| **cell_formula_units_Z**    | 8                    | 8                    | 8                    | 8                    | 8                    |
| **exptl_crystal_density_diffrn** | 2.539              | 2.602                | 2.616                | 2.739                | 2.767                |
| **chemical_formula_weight** | 983.79              | 983.79              | 983.79              | 983.79              | 983.79              |
| **exptl_crystal_F_000**     | 3712                 | 3712                 | 3712                 | 3712                 | 3712                 |
| **diffrn_ambient_temperature** | 293                | 293                  | 293                  | 293                  | 293                  |
| **cell_measurement_temperature** | 293               | 293                  | 293                  | 293                  | 293                  |
| **diffrn_reflns_theta_max** | 27.723               | 27.807               | 27.809               | 27.936               | 25.491               |
| **exptl_absorp_coefficient_mu** | 7.497             | 7.940                | 7.983                | 8.358                | 8.443                |
| **diffrn_reflns_number**   | 23039                | 24668                | 22962                | 22777                | 20731                |
| **cell_measurement_reflns_used** | 6353               | 6462                 | 5891                 | 6420                 | 6082                 |
| **refine_ls_R_factor_gt**  | 0.0436               | 0.0643               | 0.0845               | 0.0660               | 0.0702               |
| **refine_ls_wR_factor_ref** | 0.0997               | 0.1548               | 0.2092               | 0.1573               | 0.1660               |
| **refine_ls_number_parameters** | 274                | 274                  | 274                  | 274                  | 274                  |
| **refine_ls_number_restraints** | 372                | 385                  | 441                  | 87                   | 87                   |
| **refine_ls_goodness_of_fit_ref** | 1.053             | 1.017                | 1.073                | 1.045                | 1.139                |
| Experiment number - Pressure | Exp. 7.5 – 34.3 kbar | Exp. 2.4 – 41.2 kbar | Exp. 7.6 – 48.7 kbar | Exp. 2.5 – 53.7 kbar | Exp. 7.7 – 58.6 kbar |
|-----------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| **chemical_formula_sum**    | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}AgAuCl\textsubscript{10}S\textsubscript{3} |
| **exptl_crystal_colour**    | yellow               | yellow               | yellow               | orange               | orange               |
| **exptl_crystal_description** | prism               | prism               | prism               | prism               | prism               |
| **exptl_crystal_size_max**  | 0.09                 | 0.163               | 0.09                 | 0.12                 | 0.09                 |
| **exptl_crystal_size_mid**  | 0.08                 | 0.06                | 0.08                 | 0.06                 | 0.08                 |
| **exptl_crystal_size_min**  | 0.013                | 0.03                | 0.013                | 0.03                 | 0.013                |
| **space_group_crystal_system** | monoclinic          | monoclinic          | monoclinic          | monoclinic          | monoclinic          |
| **space_group_name_H-M_alt** | C 1 2/c 1           | C 1 2/c 1           | C 1 2/c 1           | C 1 2/c 1           | C 1 2/c 1           |
| **cell_length_a**           | 22.1408(17)          | 21.847(10)          | 21.7321(19)         | 21.442(5)           | 21.422(3)           |
| **cell_length_b**           | 8.00587(18)          | 7.9419(8)           | 7.9142(2)           | 7.8469(4)           | 7.8628(3)           |
| **cell_length_c**           | 27.327(9)            | 27.48(5)            | 27.073(10)          | 26.97(3)            | 26.913(14)          |
| **cell_angle_alpha**        | 90                   | 90                  | 90                   | 90                   | 90                   |
| **cell_angle_beta**         | 109.65(2)            | 109.36(12)          | 109.52(2)           | 109.32(6)           | 109.29(3)           |
| **cell_angle_gamma**        | 90                   | 90                  | 90                   | 90                   | 90                   |
| **cell_volume**             | 4561.9(16)           | 4498(9)             | 4388.5(18)          | 4283(5)             | 4279(2)             |
| **cell_formula_units_Z**    | 8                    | 8                   | 8                    | 8                    | 8                    |
| **exptl_crystal_density_diffn** | 2.865                | 2.905               | 2.978                | 3.052                | 3.055                |
| **chemical_formula_weight** | 983.79               | 983.79              | 983.79              | 983.79              | 983.79              |
| **exptl_crystal_F_000**     | 3712                 | 3712                | 3712                 | 3712                 | 3712                 |
| **diffrn_ambient_temperature** | 293                 | 293                 | 293                  | 293                  | 293                  |
| **cell_measurement_temperature** | 293                 | 293                 | 293                  | 293                  | 293                  |
| **diffrn_reflns_theta_max** | 27.715               | 27.920              | 27.850               | 27.932               | 27.733               |
| **exptl_absorpt_coefficient_mu** | 8.742               | 8.866               | 9.087                | 9.312                | 9.321                |
| **diffrn_reflns_number**   | 21727                | 22827               | 20853                | 19023                | 20316                |
| **cell_measurement_reflns_used** | 6017                | 8121               | 5615                 | 4679                 | 5820                 |
| **refine_ls_R_factor_gt**  | 0.0580               | 0.0842              | 0.0601               | 0.0756               | 0.0667               |
| **refine_ls_wR_factor_ref** | 0.1262              | 0.2376              | 0.1440               | 0.2265               | 0.1583               |
| **refine_ls_number_parameters** | 388                 | 456                 | 408                  | 455                  | 408                  |
| **refine_ls_number_restraints** | 417                 | 665                 | 441                 | 690                 | 456                  |
| **refine_ls_goodness_of_fit_ref** | 1.063               | 1.060              | 1.053               | 1.062               | 1.071               |
| Experiment number - Pressure | Exp. 2.6 – 66.9 kbar | Exp. 7.8 – 74.8 kbar | Exp. 7.9A – 100.3 kbar | Exp. 7.10 – 129.1 kbar | Exp. 7.11 – 149.4 kbar |
|-------------------------------|----------------------|----------------------|------------------------|------------------------|------------------------|
| chemical_formula_sum         | C\textsubscript{18}H\textsubscript{12}Ag Au Cl\textsubscript{10} S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}Ag Au Cl\textsubscript{10} S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}Ag Au Cl\textsubscript{10} S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}Ag Au Cl\textsubscript{10} S\textsubscript{3} | C\textsubscript{18}H\textsubscript{12}Ag Au Cl\textsubscript{10} S\textsubscript{3} |
| expltl_crystal_colour        | orange               | orange               | brown                  | brown                  | brown                  |
| expltl_crystal_description   | prism                | prism                | prism                  | prism                  | prism                  |
| expltl_crystal_size_max      | 0.12                 | 0.09                 | 0.09                   | 0.09                   | 0.09                   |
| expltl_crystal_size_mid      | 0.06                 | 0.08                 | 0.08                   | 0.08                   | 0.08                   |
| expltl_crystal_size_min      | 0.03                 | 0.013                | 0.013                  | 0.013                  | 0.013                  |
| space_group_crystal_system   | monoclinic           | monoclinic           | monoclinic             | monoclinic             | monoclinic             |
| space_group_name_H-M_alt     | C 1 2/c 1            | C 1 2/c 1            | C 1 2/c 1              | C 1 2/c 1              | C 1 2/c 1              |
| space_group_name_Hall        | -C 2yc               | -C 2yc               | -C 2yc                 | -C 2yc                 | -C 2yc                 |
| cell_length_a                | 21.220(3)            | 21.089(3)            | 20.617(5)              | 20.323(5)              | 19.980(15)             |
| cell_length_b                | 7.8301(4)            | 7.7928(3)            | 7.7051(6)              | 7.6796(5)              | 7.6558(14)             |
| cell_length_c                | 26.741(16)           | 26.668(15)           | 26.32(3)               | 25.76(3)               | 25.58(8)               |
| cell_angle_alpha             | 90                   | 90                   | 90                     | 90                     | 90                     |
| cell_angle_beta              | 108.99(4)            | 108.98(3)            | 108.30(7)              | 108.22(6)              | 108.21(18)             |
| cell_angle_gamma             | 90                   | 90                   | 90                     | 90                     | 90                     |
| cell_volume                  | 4201(3)              | 4144(3)              | 3970(5)                | 3818(4)                | 3716(12)               |
| cell_formula_units_Z         | 8                    | 8                    | 8                      | 8                      | 8                      |
| exptl_crystal_density_diffrn | 3.111                | 3.154                | 3.292                  | 3.423                  | 3.516                  |
| chemical_formula_weight      | 983.79               | 983.79               | 983.79                 | 983.79                 | 983.79                 |
| exptl_crystal_F_000          | 3712                 | 3712                 | 3712                   | 3712                   | 3712                   |
| diffrn_ambient_temperature  | 293                  | 293                  | 293                    | 293                    | 293                    |
| cell_measurement_temperature | 293                  | 293                  | 293                    | 293                    | 293                    |
| diffrn_reflns_theta_max      | 27.871               | 24.561               | 25.459                 | 27.866                 | 28.172                 |
| exptl_absorp_coefficient_mu  | 9.492                | 9.623                | 10.046                 | 10.445                 | 10.729                 |
| diffrn_reflns_number         | 19527                | 12953                | 15749                  | 17628                  | 16751                  |
| cell_measurement_reflns_used | 4078                 | 4292                 | 4760                   | 2653                   | 1603                   |
| refine_ls_R_factor_gt        | 0.0821               | 0.0656               | 0.1258                 | 0.1576                 | 0.2756                 |
| refine_ls_wR_factor_ref      | 0.2010               | 0.1416               | 0.3555                 | 0.4521                 | 0.6204                 |
| refine_ls_number_parameters  | 408                  | 408                  | 338                    | 436                    | 351                    |
| refine_ls_number_restraints  | 489                  | 456                  | 423                    | 1027                   | 729                    |
| refine_ls_goodness_of_fit_ref | 1.072               | 1.054                | 1.343                  | 1.642                  | 2.003                  |
| Experiment number - Pressure | Exp. 7.12 – 96.4 kbar | Exp. 7.14 – 24.7 kbar | Exp. 7.15 – 14.3 kbar | Exp. 7.16 – 10.0 kbar | Exp. 7.17 – 5.25 kbar |
|-----------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| chemical_formula_sum        | C_{18}H_{12}AgAuCl_{10}S_{3} | C_{18}H_{12}AgAuCl_{10}S_{3} | C_{18}H_{12}AgAuCl_{10}S_{3} | C_{18}H_{12}AgAuCl_{10}S_{3} | C_{18}H_{12}AgAuCl_{10}S_{3} |
| expl_crystal_colour         | brown                 | dark green            | dark green            | prism                 | green                |
| expl_crystal_description    | prism                 | prism                 | prism                 | prism                 | prism                |
| expl_crystal_size_max       | 0.13                  | 0.09                  | 0.09                  | 0.09                  | 0.09                 |
| expl_crystal_size_mid       | 0.08                  | 0.08                  | 0.08                  | 0.08                  | 0.08                 |
| expl_crystal_size_min       | 0.0013                | 0.013                | 0.013                | 0.013                | 0.013                |
| space_group_crystal_system  | monoclinic            | monoclinic            | monoclinic            | monoclinic            | triclinic            |
| space_group_name_H-M_alt    | C 1 2/c 1             | C 1 2/c 1             | C 1 2/c 1             | C 1 2/c 1             | P -1                 |
| space_group_name_Hall       | -C 2yc                | -C 2yc                | -C 2yc                | -C 2yc                | -P 1                 |
| cell_length_a               | 20.473(11)            | 22.549(6)             | 23.003(5)             | 23.212(5)             | 8.6157(16)           |
| cell_length_b               | 7.7638(8)             | 8.1533(5)             | 8.3280(4)             | 8.4325(5)             | 12.541(3)            |
| cell_length_c               | 26.41(6)              | 27.46(3)              | 27.64(2)              | 27.77(2)              | 26.548(7)            |
| cell_angle_alpha            | 90                    | 90                    | 90                    | 90                    | 90.73(2)             |
| cell_angle_beta             | 108.22(13)            | 109.78(6)             | 110.03(5)             | 110.12(6)             | 99.12(2)             |
| cell_angle_gamma            | 90                    | 90                    | 90                    | 90                    | 110.059(19)          |
| cell_volume                 | 3987(9)               | 4751(5)               | 4974(4)               | 5104(5)               | 2653.5(11)           |
| cell_formula_units_Z        | 8                     | 8                     | 8                     | 8                     | 4                    |
| expl_crystal_density_diffrn | 3.278                 | 2.751                 | 2.627                 | 2.561                 | 2.463                |
| chemical_formula_weight     | 983.79                | 983.79                | 983.79                | 983.79                | 983.79               |
| expl_crystal_F_000          | 3712                  | 3712                  | 3712                  | 3712                  | 1856                 |
| diffrn_ambient_temperature | 293                   | 293(2)                | 293(2)                | 293                   | 293                  |
| cell_measurement_temperature | 293                 | 293                   | 293                   | 293                   | 293                  |
| diffrn_reflns_theta_max     | 27.711                | 27.956                | 27.741                | 27.872                | 27.972               |
| expl_absort_coefficient_mu  | 10.002                | 8.394                 | 8.017                 | 7.813                 | 7.515                |
| diffrn_reflns_number        | 17911                 | 21936                 | 22307                 | 23191                 | 23256                |
| cell_measurement_reflns_used | 2329                | 3670                  | 3787                  | 3388                  | 2522                 |
| refine_ls_R_factor_gt       | 0.1867                | 0.1187                | 0.0932                | 0.1233                | 0.1894               |
| refine_ls_wR_factor_ref     | 0.4777                | 0.2350                | 0.1625                | 0.2301                | 0.4259               |
| refine_ls_number_parameters | 446                   | 298                   | 298                   | 298                   | 507                  |
| refine_ls_number_restraints | 1048                  | 603                   | 597                   | 638                   | 951                  |
| refine_ls_goodness_of_fit_ref | 1.659              | 1.084                 | 1.154                 | 1.198                 | 1.035                |
2. Photophysical properties at different pressures and ambient temperature.

Fig. S15. Normalised emission spectra of $E$-[Au(C₆Cl₅)₂Ag([9]aneS₃)]₂ single crystal at pressures between ambient and 103.5 kbar of pressure.
Fig. S16. Optimized model $E-S_0$ in the ground state (left) and model $E-T_1$ in the triplet excited state (right), and the corresponding MO diagram for each model.
2.1. Mathematical treatment of the exponential functions found experimentally.

Mathematically, the exponential functions that fit the experimental results, as well the theoretical treatment of the repulsive branch of the potential energy curve, can be generalized with the expression: \( y = y_0 + A \cdot e^{r_0 x} \)

where \( y \) is the parameter represented versus the Au···Au distance (x),
\( y_0 \) is the value of this parameter at the equilibrium Au···Au distance at ambient pressure,
\( A \) is the initial value, i.e. \( y-y_0 \) when \( x = 0 \),
\( r_0 \) is the rate,

and

Reasoning mathematically:

\( r_0 = \ln(y-y_0/A)/x \)

Since the \( r_0 \) values are roughly similar for the three exponential representations,

\( \ln(p-p_0/A_1) = \ln(em-em_0/A_2) = \ln(S-S_0/A_3) \),

which is the symmetrical representation of a straight line in three-dimensional space with an approximate slope of 5 for each projection. This demonstrates mathematically that under the applied pressures the experimental Au···Au distances vary exponentially, and that the energy of the emissions and the total repulsive potential energy computed vary following the same trend.

On the other hand, taking into account that the straight-line expression that relates potential energy and experimental energy emission takes the form of:

\( S_0 = -2.513571 \cdot 10^8 - 2.15343771 \cdot E_{em} \)

Since at the point where both states cross each other \( E_{em} = 0 \),

i.e. \( S_0 = T_1 = -2.513571 \cdot 10^8 \) cm\(^{-1}\).

Introducing this value in the straight line equation that relates potential energy versus pressure:

\( P = 4.403429 \cdot 10^6 + 0.0175157 \cdot S_0 \)

gives a value of \( P = 733 \) kbar

and introducing this one in the equation that relates pressure and Au···Au distances:

\( P = -4.17944610 + 1.87483657 \cdot 10^8 \cdot e^{-5.10(d(Au···Au))} \)

we obtain a value for \( d(Au···Au) \) of 2.438 Å.
**Fig. S17.** Computed potential energy of the ground state $S_0$ using pseudo-relativistic pseudopotentials for gold vs Au···Au distance.

**Fig. S18.** Computed potential energy of the ground state $S_0$ using non-relativistic pseudopotentials for gold vs Au···Au distance.
**Fig. S19.** $S_0$ energy calculated with non-relativistic pseudopotentials - $S_0$ energy calculated with pseudo-relativistic pseudopotentials for Au···Au distances in the range 2.44–3.40 Å.