# metal-organic compounds

# [μ-1,1′-Bis(diphenylphosphino)-ferrocene]bis{[(Z)-O-ethyl N-phenylthio-carbamato-κS]gold(I)} dichloromethane solvate

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The binuclear title compound, $[Au_2Fe(C_9H_{10}NOS)_2(C_{17}H_{14}P)_2]\cdot CH_2Cl_2$, which has the Fe atom located on a crystallographic centre of inversion, crystallizes as a 1:1 dichloromethane solvate, which is disordered about a centre of inversion. There is a small deviation from linearity defined by the $SP$ donor set [S1—Au—P1 angle is 175.35 (5) °] which is due to an intramolecular Au···O contact [3.080 (5) Å]. The primary intermolecular contacts between binuclear molecules are of the type C—H···$\pi$, and are arranged so as to form columns in the $a$-axis direction in which the disordered solvent molecules reside.

## Related literature

For the structural systematics and luminescence properties of phosphinegold(I) carbonimidothioates, see: Ho *et al.* (2006); Ho & Tiekink (2007); Kuan *et al.* (2008). For the synthesis, see: Hall *et al.* (1993). For related structures, see: Ho & Tiekink (2009); Tadbuppa & Tiekink (2009).
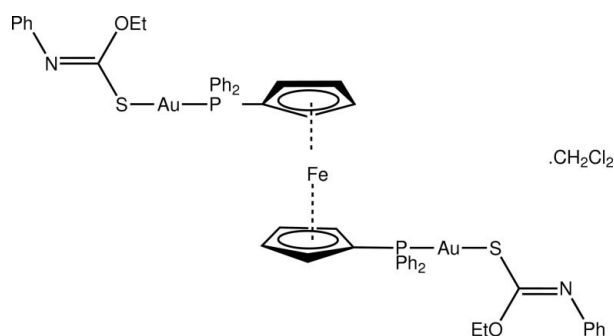


## Experimental

### Crystal data

| | |
|---|---|
| $[Au_2Fe(C_9H_{10}NOS)_2(C_{17}H_{14}P)_2]\cdot CH_2Cl_2$ | $\beta = 103.177\ (8)°$ |
| $M_r = 1393.69$ | $\gamma = 106.853\ (8)°$ |
| Triclinic, $P\bar{1}$ | $V = 1253.5\ (9)$ Å$^3$ |
| $a = 8.442\ (3)$ Å | $Z = 1$ |
| $b = 12.957\ (5)$ Å | Mo $K\alpha$ radiation |
| $c = 13.440\ (5)$ Å | $\mu = 6.42$ mm$^{-1}$ |
| $\alpha = 108.045\ (8)°$ | $T = 223$ K |
| | $0.49 \times 0.04 \times 0.04$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD diffractometer | 8618 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2000) | 5688 independent reflections |
| | 5025 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.577$, $T_{max} = 1$ | $R_{int} = 0.030$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | 13 restraints |
| $wR(F^2) = 0.106$ | H-atom parameters constrained |
| $S = 1.02$ | $\Delta\rho_{max} = 2.84$ e Å$^{-3}$ |
| 5688 reflections | $\Delta\rho_{min} = -1.47$ e Å$^{-3}$ |
| 307 parameters | |

**Table 1**
Selected bond lengths (Å).

| Au—P1 | 2.2562 (15) | Au—S1 | 2.3029 (16) |
|---|---|---|---|

**Table 2**
Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the C2–C7 and C15–C20 rings, respectively.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C9—H9a···$Cg1$[i] | 0.97 | 2.75 | 3.623 (9) | 150 |
| C11—H11···$Cg2$[ii] | 0.94 | 2.78 | 3.619 (7) | 150 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y, -z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## References

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**supplementary materials**

# [μ-1,1'-Bis(diphenylphosphino)ferrocene]bis{[(*Z*)-*O*-ethyl *N*-phenylthiocarbamato-*κS*]gold(I)} dichloromethane solvate

## S. Y. Ho and E. R. T. Tiekink

## Comment

The dppf (where dppf is the bidentate phosphine, $[Ph_2P(C_5H_4)]_2Fe$) derivatives of phosphinegold(I) thiocarbamides, of interest owing to crystal engineering and luminescence studies (Ho *et al.* 2006; Ho & Tiekink, 2007; Kuan *et al.*, 2008), are comparatively rare. Thus, only three examples of dppf{Au[SC(OR)=NR']}$_2$ have been described, i.e. R = Me & R' = PhNO$_2$-4 (Ho *et al.*, 2006), R = iPr & R' = PhNO$_2$-4 (Ho & Tiekink, 2009), and R = iPr & R' = PhMe-4 (Tadbuppa & Tiekink, 2009). In the present report, the crystal structure of the R = Et & R' = H derivative, (I), is described.

The dinuclear molecule has crystallographic symmetry with the Fe atom lying on an inversion centre, Fig. 1. The dinuclear molecule crystallises with a solvent dichloromethane molecule which is disordered about a centre of inversion, Fig. 1. The gold atom exists in the expected linear geometry defined by a *SP* donor set, Table 1, and the deviation from linearity [S1–Au–P1 is 175.35 (5) °] is ascribed to the close approach of the O1 atom, Au⋯O = 3.080 (5) Å. The anion, with a Z configuration about the C1=N1 bond, shows the expected characteristics. The magnitudes of the C1—S1 and C1=N1 bond distances of 1.755 (6) and 1.277 (8) Å, respectively, confirm that the anion is coordinating as a thiolate ligand. The overall conformation of the molecule is "open" in that the thiocarbamate ligands are lying on either side of the molecule, as found in the structure of the R = iPr & R' = PhMe-4 derivative (Tadbuppa & Tiekink, 2009) but contrasts the situation in each of dppf{Au[SC(OR)= NC$_6$H$_4$NO$_2$-p]}$_2$, for R = Me (Ho *et al.*, 2006) and i-Pr (Ho & Tiekink, 2009), whereby the molecule has a U-shaped conformation allowing for the formation of intramolecular Au⋯Au interactions.

In the crystal structure of (I), the primary interactions between the dinuclear molecules are of the type C–H⋯π, Table 1. These are arranged so as to define columns along the *a* direction in which reside the solvent dichloromethane molecules.

## Experimental

Compound (I) was prepared following the standard literature procedure from the reaction of dppf(AuCl)$_2$ and EtOC(=S)N(H)Ph in the presence of base (Hall *et al.*, 1993). Crystals were obtained from the slow evaporation of a dichloromethane solution.

## Refinement

The H atoms were geometrically placed (C—H = 0.94-0.98 Å) and refined as riding with $U_{iso}(H) = 1.2\text{-}1.5U_{eq}(C)$. The maximum and minimum residual electron density peaks of 2.84 and 1.47 e Å$^{-3}$, respectively, were located within the C21–C26 ring (0.95 Å from the C21 atom) and 0.58 Å from the Cl1 atom, respectively. The binuclear molecule co-crystallised with a disordered dichloromethane solvent molecule. This was modelled over a centre of inversion with a full weight chloride and half-weight methylene group. The C and Cl atoms were treated with the ISOR command in SHELXL-97 to impose

# supplementary materials

isotropic character to the anisotropic displacement parameters (Sheldrick, 2008). The following reflections (0,1,0), (0,-1,1) and (0,0,1) were omitted in the final refinement as they were obscured by the beamstop.
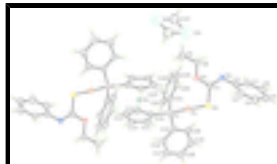
**Figures**



Fig. 1. Molecular structure of the dinuclear complex (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level. The dinuclear molecule is located about a centre of inversion and unlabelled atoms are related by the symmetry operation -*x*, -*y*, -*z*. Also shown is the solvent dichloromethane molecule which is disordered about a centre of inversion. Unlabelled atoms are related by -*x*, 1-*y*, 1-*z* for this molecule.
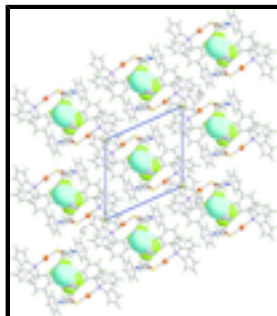


Fig. 2. A view in projection down the *a* axis of the crystal packing in (I) highlighting the interactions between binuclear molecules mediated by C–H···π contacts (purple dashed lines). The binuclear molecules define columns in which reside the disordered dichloromethane molecules, shown in space filling mode. Colour code: Au, orange; Fe, olive green; S, yellow; P, pink; O, red; N, blue; C, grey; and H, green.

**[μ-1,1'-Bis(diphenylphosphino)ferrocene]bis{[(*Z*)-*O*-ethyl *N*-phenylthiocarbamato-κ*S*]gold(I)} dichloromethane solvate**

*Crystal data*

| | |
|---|---|
| $[Au_2Fe(C_9H_{10}NOS)_2(C_{17}H_{14}P)_2]·CH_2Cl_2$ | $Z = 1$ |
| $M_r = 1393.69$ | $F(000) = 678$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.846$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å |
| $a = 8.442$ (3) Å | Cell parameters from 4599 reflections |
| $b = 12.957$ (5) Å | $\theta = 2.6–30.1°$ |
| $c = 13.440$ (5) Å | $\mu = 6.42$ mm$^{-1}$ |
| $\alpha = 108.045$ (8)° | $T = 223$ K |
| $\beta = 103.177$ (8)° | Needle, orange |
| $\gamma = 106.853$ (8)° | $0.49 \times 0.04 \times 0.04$ mm |
| $V = 1253.5$ (9) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD diffractometer | 5688 independent reflections |
| Radiation source: fine-focus sealed tube | 5025 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.030$ |
| ω scans | $\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $h = -10 \rightarrow 10$ |
| $T_{min} = 0.577$, $T_{max} = 1$ | $k = -16 \rightarrow 11$ |

8618 measured reflections

$l = -16 \rightarrow 17$

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.106$ | H-atom parameters constrained |
| $S = 1.02$ | $w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 5688 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 307 parameters | $\Delta\rho_{max} = 2.84$ e Å$^{-3}$ |
| 13 restraints | $\Delta\rho_{min} = -1.47$ e Å$^{-3}$ |

*Special details*

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

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Au | 0.54576 (2) | 0.149128 (17) | 0.224945 (16) | 0.02842 (9) | |
| Fe | 0.0000 | 0.0000 | 0.0000 | 0.0234 (2) | |
| S1 | 0.6884 (2) | 0.11576 (15) | 0.37230 (12) | 0.0387 (3) | |
| P1 | 0.42701 (17) | 0.19357 (11) | 0.08358 (11) | 0.0240 (3) | |
| O1 | 0.4392 (5) | 0.1685 (4) | 0.4324 (3) | 0.0397 (10) | |
| N1 | 0.6859 (6) | 0.2200 (5) | 0.5809 (4) | 0.0368 (11) | |
| C1 | 0.6054 (8) | 0.1739 (5) | 0.4754 (5) | 0.0317 (11) | |
| C2 | 0.8589 (8) | 0.2308 (5) | 0.6274 (5) | 0.0344 (12) | |
| C3 | 0.8983 (9) | 0.1323 (6) | 0.6232 (6) | 0.0422 (14) | |
| H3 | 0.8092 | 0.0561 | 0.5840 | 0.051* | |
| C4 | 1.0693 (9) | 0.1475 (6) | 0.6769 (6) | 0.0439 (14) | |
| H4 | 1.0952 | 0.0810 | 0.6739 | 0.053* | |
| C5 | 1.2007 (9) | 0.2566 (6) | 0.7341 (5) | 0.0434 (15) | |
| H5 | 1.3163 | 0.2649 | 0.7690 | 0.052* | |
| C6 | 1.1636 (8) | 0.3563 (6) | 0.7409 (6) | 0.0440 (15) | |
| H6 | 1.2529 | 0.4323 | 0.7808 | 0.053* | |
| C7 | 0.9909 (8) | 0.3404 (6) | 0.6873 (5) | 0.0394 (13) | |

| | | | | |
|---|---|---|---|---|
| H7 | 0.9642 | 0.4070 | 0.6924 | 0.047* |
| C8 | 0.3614 (8) | 0.2141 (7) | 0.5128 (6) | 0.0466 (16) |
| H8A | 0.4412 | 0.2944 | 0.5658 | 0.056* |
| H8B | 0.3408 | 0.1646 | 0.5546 | 0.056* |
| C9 | 0.1920 (10) | 0.2139 (8) | 0.4508 (6) | 0.0551 (19) |
| H9A | 0.1370 | 0.2436 | 0.5031 | 0.083* |
| H9B | 0.1142 | 0.1342 | 0.3983 | 0.083* |
| H9C | 0.2139 | 0.2640 | 0.4106 | 0.083* |
| C10 | 0.2261 (7) | 0.0814 (4) | −0.0219 (4) | 0.0255 (10) |
| C11 | 0.1892 (7) | −0.0416 (5) | −0.0552 (5) | 0.0312 (11) |
| H11 | 0.2615 | −0.0753 | −0.0247 | 0.037* |
| C12 | 0.0209 (8) | −0.1038 (5) | −0.1443 (5) | 0.0377 (14) |
| H12 | −0.0363 | −0.1860 | −0.1833 | 0.045* |
| C13 | −0.0434 (8) | −0.0202 (5) | −0.1629 (5) | 0.0372 (13) |
| H13 | −0.1520 | −0.0377 | −0.2161 | 0.045* |
| C14 | 0.0802 (7) | 0.0937 (5) | −0.0894 (5) | 0.0304 (11) |
| H14 | 0.0693 | 0.1650 | −0.0853 | 0.036* |
| C15 | 0.5783 (7) | 0.2270 (4) | 0.0097 (5) | 0.0268 (10) |
| C16 | 0.5327 (8) | 0.1678 (5) | −0.1046 (5) | 0.0320 (11) |
| H16 | 0.4185 | 0.1101 | −0.1479 | 0.038* |
| C17 | 0.6581 (9) | 0.1949 (6) | −0.1545 (5) | 0.0395 (13) |
| H17 | 0.6282 | 0.1551 | −0.2319 | 0.047* |
| C18 | 0.8269 (8) | 0.2804 (6) | −0.0905 (6) | 0.0426 (15) |
| H18 | 0.9102 | 0.2990 | −0.1247 | 0.051* |
| C19 | 0.8716 (8) | 0.3371 (6) | 0.0215 (6) | 0.0425 (14) |
| H19 | 0.9861 | 0.3945 | 0.0643 | 0.051* |
| C20 | 0.7489 (7) | 0.3110 (5) | 0.0738 (5) | 0.0335 (12) |
| H20 | 0.7812 | 0.3498 | 0.1515 | 0.040* |
| C21 | 0.3847 (7) | 0.3269 (5) | 0.1315 (5) | 0.0294 (11) |
| C22 | 0.3700 (7) | 0.3903 (5) | 0.0660 (5) | 0.0321 (11) |
| H22 | 0.3774 | 0.3630 | −0.0056 | 0.038* |
| C23 | 0.3444 (8) | 0.4938 (5) | 0.1063 (6) | 0.0372 (13) |
| H23 | 0.3335 | 0.5363 | 0.0615 | 0.045* |
| C24 | 0.3348 (8) | 0.5355 (5) | 0.2118 (6) | 0.0379 (13) |
| H24 | 0.3199 | 0.6068 | 0.2393 | 0.046* |
| C25 | 0.3471 (9) | 0.4717 (6) | 0.2762 (6) | 0.0454 (15) |
| H25 | 0.3379 | 0.4988 | 0.3473 | 0.055* |
| C26 | 0.3728 (8) | 0.3689 (5) | 0.2371 (5) | 0.0353 (12) |
| H26 | 0.3824 | 0.3265 | 0.2821 | 0.042* |
| Cl1 | 0.1902 (6) | 0.5357 (4) | 0.5501 (4) | 0.1365 (14) |
| C27 | 0.0112 (19) | 0.5715 (19) | 0.548 (2) | 0.085 (6) | 0.50 |
| H27A | 0.0327 | 0.6434 | 0.5342 | 0.103* | 0.50 |
| H27B | 0.0018 | 0.5900 | 0.6223 | 0.103* | 0.50 |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Au | 0.02700 (12) | 0.03400 (13) | 0.02496 (13) | 0.01353 (9) | 0.00771 (8) | 0.01222 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Fe | 0.0212 (4) | 0.0246 (5) | 0.0227 (5) | 0.0075 (4) | 0.0068 (4) | 0.0093 (4) |
| S1 | 0.0421 (8) | 0.0566 (9) | 0.0265 (7) | 0.0317 (7) | 0.0117 (6) | 0.0171 (6) |
| P1 | 0.0230 (6) | 0.0252 (6) | 0.0242 (6) | 0.0100 (5) | 0.0086 (5) | 0.0098 (5) |
| O1 | 0.031 (2) | 0.054 (3) | 0.028 (2) | 0.0181 (19) | 0.0081 (17) | 0.0088 (19) |
| N1 | 0.031 (2) | 0.049 (3) | 0.021 (2) | 0.010 (2) | 0.0066 (19) | 0.009 (2) |
| C1 | 0.032 (3) | 0.037 (3) | 0.026 (3) | 0.015 (2) | 0.009 (2) | 0.013 (2) |
| C2 | 0.033 (3) | 0.049 (3) | 0.023 (3) | 0.016 (2) | 0.011 (2) | 0.016 (2) |
| C3 | 0.041 (3) | 0.040 (3) | 0.040 (3) | 0.009 (3) | 0.010 (3) | 0.019 (3) |
| C4 | 0.051 (4) | 0.048 (4) | 0.042 (4) | 0.025 (3) | 0.013 (3) | 0.027 (3) |
| C5 | 0.035 (3) | 0.064 (4) | 0.033 (3) | 0.021 (3) | 0.009 (3) | 0.023 (3) |
| C6 | 0.030 (3) | 0.051 (4) | 0.038 (3) | 0.007 (3) | 0.007 (3) | 0.015 (3) |
| C7 | 0.031 (3) | 0.047 (3) | 0.038 (3) | 0.015 (3) | 0.012 (3) | 0.014 (3) |
| C8 | 0.037 (3) | 0.061 (4) | 0.036 (3) | 0.022 (3) | 0.014 (3) | 0.007 (3) |
| C9 | 0.052 (4) | 0.083 (5) | 0.037 (4) | 0.042 (4) | 0.016 (3) | 0.018 (4) |
| C10 | 0.026 (2) | 0.026 (2) | 0.025 (2) | 0.0100 (19) | 0.008 (2) | 0.0101 (19) |
| C11 | 0.034 (3) | 0.027 (3) | 0.034 (3) | 0.013 (2) | 0.015 (2) | 0.011 (2) |
| C12 | 0.033 (3) | 0.032 (3) | 0.035 (3) | 0.003 (2) | 0.018 (3) | 0.002 (2) |
| C13 | 0.032 (3) | 0.046 (3) | 0.023 (3) | 0.007 (2) | 0.006 (2) | 0.011 (2) |
| C14 | 0.026 (2) | 0.041 (3) | 0.027 (3) | 0.012 (2) | 0.010 (2) | 0.019 (2) |
| C15 | 0.024 (2) | 0.028 (2) | 0.035 (3) | 0.012 (2) | 0.013 (2) | 0.017 (2) |
| C16 | 0.032 (3) | 0.033 (3) | 0.034 (3) | 0.013 (2) | 0.012 (2) | 0.015 (2) |
| C17 | 0.049 (3) | 0.049 (3) | 0.037 (3) | 0.027 (3) | 0.027 (3) | 0.022 (3) |
| C18 | 0.038 (3) | 0.053 (4) | 0.065 (4) | 0.028 (3) | 0.033 (3) | 0.040 (3) |
| C19 | 0.027 (3) | 0.040 (3) | 0.061 (4) | 0.011 (2) | 0.016 (3) | 0.022 (3) |
| C20 | 0.027 (3) | 0.032 (3) | 0.038 (3) | 0.008 (2) | 0.010 (2) | 0.013 (2) |
| C21 | 0.020 (2) | 0.028 (2) | 0.035 (3) | 0.0059 (19) | 0.008 (2) | 0.010 (2) |
| C22 | 0.030 (3) | 0.027 (3) | 0.038 (3) | 0.011 (2) | 0.013 (2) | 0.011 (2) |
| C23 | 0.028 (3) | 0.035 (3) | 0.048 (4) | 0.012 (2) | 0.011 (3) | 0.019 (3) |
| C24 | 0.034 (3) | 0.026 (3) | 0.044 (3) | 0.010 (2) | 0.009 (3) | 0.005 (2) |
| C25 | 0.048 (4) | 0.047 (4) | 0.032 (3) | 0.019 (3) | 0.016 (3) | 0.003 (3) |
| C26 | 0.038 (3) | 0.032 (3) | 0.035 (3) | 0.014 (2) | 0.015 (3) | 0.011 (2) |
| Cl1 | 0.1389 (16) | 0.1335 (16) | 0.1363 (16) | 0.0487 (10) | 0.0470 (10) | 0.0583 (10) |
| Cl1' | 0.1389 (16) | 0.1335 (16) | 0.1363 (16) | 0.0487 (10) | 0.0470 (10) | 0.0583 (10) |
| C27 | 0.086 (6) | 0.085 (6) | 0.085 (6) | 0.033 (2) | 0.030 (2) | 0.035 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Au—P1 | 2.2562 (15) | C9—H9C | 0.9700 |
| Au—S1 | 2.3029 (16) | C10—C11 | 1.429 (7) |
| Fe—C10 | 2.030 (5) | C10—C14 | 1.435 (7) |
| Fe—C10[i] | 2.030 (5) | C11—C12 | 1.437 (8) |
| Fe—C14[i] | 2.043 (5) | C11—H11 | 0.9400 |
| Fe—C14 | 2.043 (5) | C12—C13 | 1.405 (9) |
| Fe—C11[i] | 2.046 (5) | C12—H12 | 0.9400 |
| Fe—C11 | 2.046 (5) | C13—C14 | 1.406 (8) |
| Fe—C13[i] | 2.054 (6) | C13—H13 | 0.9400 |
| Fe—C13 | 2.054 (6) | C14—H14 | 0.9400 |
| Fe—C12 | 2.068 (5) | C15—C16 | 1.387 (8) |

| | | | |
|---|---|---|---|
| Fe—C12[i] | 2.068 (5) | C15—C20 | 1.395 (7) |
| S1—C1 | 1.755 (6) | C16—C17 | 1.396 (8) |
| P1—C10 | 1.788 (5) | C16—H16 | 0.9400 |
| P1—C21 | 1.817 (5) | C17—C18 | 1.391 (9) |
| P1—C15 | 1.824 (5) | C17—H17 | 0.9400 |
| O1—C1 | 1.362 (7) | C18—C19 | 1.357 (10) |
| O1—C8 | 1.449 (7) | C18—H18 | 0.9400 |
| N1—C1 | 1.277 (7) | C19—C20 | 1.399 (8) |
| N1—C2 | 1.398 (7) | C19—H19 | 0.9400 |
| C2—C7 | 1.368 (9) | C20—H20 | 0.9400 |
| C2—C3 | 1.398 (9) | C21—C22 | 1.387 (8) |
| C3—C4 | 1.384 (9) | C21—C26 | 1.393 (8) |
| C3—H3 | 0.9400 | C22—C23 | 1.382 (8) |
| C4—C5 | 1.360 (10) | C22—H22 | 0.9400 |
| C4—H4 | 0.9400 | C23—C24 | 1.383 (9) |
| C5—C6 | 1.397 (10) | C23—H23 | 0.9400 |
| C5—H5 | 0.9400 | C24—C25 | 1.376 (10) |
| C6—C7 | 1.393 (9) | C24—H24 | 0.9400 |
| C6—H6 | 0.9400 | C25—C26 | 1.372 (9) |
| C7—H7 | 0.9400 | C25—H25 | 0.9400 |
| C8—C9 | 1.480 (9) | C26—H26 | 0.9400 |
| C8—H8A | 0.9800 | Cl1—C27 | 1.701 (5) |
| C8—H8B | 0.9800 | Cl1—C27[ii] | 1.74 (2) |
| C9—H9A | 0.9700 | C27—H27A | 0.9800 |
| C9—H9B | 0.9700 | C27—H27B | 0.9800 |
| | | | |
| P1—Au—S1 | 175.35 (5) | C9—C8—H8B | 110.1 |
| C10—Fe—C10[i] | 180.0 (3) | H8A—C8—H8B | 108.4 |
| C10—Fe—C14[i] | 138.7 (2) | C8—C9—H9A | 109.5 |
| C10[i]—Fe—C14[i] | 41.3 (2) | C8—C9—H9B | 109.5 |
| C10—Fe—C14 | 41.3 (2) | H9A—C9—H9B | 109.5 |
| C10[i]—Fe—C14 | 138.7 (2) | C8—C9—H9C | 109.5 |
| C14[i]—Fe—C14 | 180.0 (3) | H9A—C9—H9C | 109.5 |
| C10—Fe—C11[i] | 139.0 (2) | H9B—C9—H9C | 109.5 |
| C10[i]—Fe—C11[i] | 41.0 (2) | C11—C10—C14 | 108.0 (5) |
| C14[i]—Fe—C11[i] | 69.0 (2) | C11—C10—P1 | 122.9 (4) |
| C14—Fe—C11[i] | 111.0 (2) | C14—C10—P1 | 129.0 (4) |
| C10—Fe—C11 | 41.0 (2) | C11—C10—Fe | 70.1 (3) |
| C10[i]—Fe—C11 | 139.0 (2) | C14—C10—Fe | 69.9 (3) |
| C14[i]—Fe—C11 | 111.0 (2) | P1—C10—Fe | 127.3 (3) |
| C14—Fe—C11 | 69.0 (2) | C10—C11—C12 | 107.0 (5) |
| C11[i]—Fe—C11 | 180.0 (3) | C10—C11—Fe | 68.9 (3) |
| C10—Fe—C13[i] | 111.7 (2) | C12—C11—Fe | 70.4 (3) |
| C10[i]—Fe—C13[i] | 68.3 (2) | C10—C11—H11 | 126.5 |
| C14[i]—Fe—C13[i] | 40.1 (2) | C12—C11—H11 | 126.5 |
| C14—Fe—C13[i] | 139.9 (2) | Fe—C11—H11 | 125.8 |

| | | | |
|---|---|---|---|
| C11$^i$—Fe—C13$^i$ | 68.3 (2) | C13—C12—C11 | 108.1 (5) |
| C11—Fe—C13$^i$ | 111.7 (2) | C13—C12—Fe | 69.5 (3) |
| C10—Fe—C13 | 68.3 (2) | C11—C12—Fe | 68.7 (3) |
| C10$^i$—Fe—C13 | 111.7 (2) | C13—C12—H12 | 126.0 |
| C14$^i$—Fe—C13 | 139.9 (2) | C11—C12—H12 | 126.0 |
| C14—Fe—C13 | 40.1 (2) | Fe—C12—H12 | 127.4 |
| C11$^i$—Fe—C13 | 111.7 (2) | C14—C13—C12 | 109.3 (5) |
| C11—Fe—C13 | 68.3 (2) | C14—C13—Fe | 69.5 (3) |
| C13$^i$—Fe—C13 | 180.0 (3) | C12—C13—Fe | 70.6 (4) |
| C10—Fe—C12 | 68.4 (2) | C14—C13—H13 | 125.3 |
| C10$^i$—Fe—C12 | 111.6 (2) | C12—C13—H13 | 125.3 |
| C14$^i$—Fe—C12 | 112.2 (2) | Fe—C13—H13 | 126.1 |
| C14—Fe—C12 | 67.8 (2) | C13—C14—C10 | 107.5 (5) |
| C11$^i$—Fe—C12 | 139.1 (2) | C13—C14—Fe | 70.3 (3) |
| C11—Fe—C12 | 40.9 (2) | C10—C14—Fe | 68.9 (3) |
| C13$^i$—Fe—C12 | 140.1 (3) | C13—C14—H14 | 126.2 |
| C13—Fe—C12 | 39.9 (3) | C10—C14—H14 | 126.2 |
| C10—Fe—C12$^i$ | 111.6 (2) | Fe—C14—H14 | 126.1 |
| C10$^i$—Fe—C12$^i$ | 68.4 (2) | C16—C15—C20 | 120.0 (5) |
| C14$^i$—Fe—C12$^i$ | 67.8 (2) | C16—C15—P1 | 122.6 (4) |
| C14—Fe—C12$^i$ | 112.2 (2) | C20—C15—P1 | 117.3 (4) |
| C11$^i$—Fe—C12$^i$ | 40.9 (2) | C15—C16—C17 | 119.3 (5) |
| C11—Fe—C12$^i$ | 139.1 (2) | C15—C16—H16 | 120.3 |
| C13$^i$—Fe—C12$^i$ | 39.9 (3) | C17—C16—H16 | 120.3 |
| C13—Fe—C12$^i$ | 140.1 (3) | C18—C17—C16 | 120.4 (6) |
| C12—Fe—C12$^i$ | 180.0 (4) | C18—C17—H17 | 119.8 |
| C1—S1—Au | 102.6 (2) | C16—C17—H17 | 119.8 |
| C10—P1—C21 | 106.8 (2) | C19—C18—C17 | 120.1 (5) |
| C10—P1—C15 | 105.4 (2) | C19—C18—H18 | 119.9 |
| C21—P1—C15 | 103.4 (2) | C17—C18—H18 | 119.9 |
| C10—P1—Au | 115.79 (18) | C18—C19—C20 | 120.7 (6) |
| C21—P1—Au | 112.8 (2) | C18—C19—H19 | 119.7 |
| C15—P1—Au | 111.77 (18) | C20—C19—H19 | 119.7 |
| C1—O1—C8 | 116.2 (5) | C15—C20—C19 | 119.5 (6) |
| C1—N1—C2 | 121.6 (5) | C15—C20—H20 | 120.3 |
| N1—C1—O1 | 120.3 (5) | C19—C20—H20 | 120.3 |
| N1—C1—S1 | 126.6 (5) | C22—C21—C26 | 119.1 (5) |
| O1—C1—S1 | 113.1 (4) | C22—C21—P1 | 121.0 (4) |
| C7—C2—N1 | 119.6 (6) | C26—C21—P1 | 119.8 (5) |
| C7—C2—C3 | 118.6 (6) | C23—C22—C21 | 119.7 (6) |
| N1—C2—C3 | 121.5 (6) | C23—C22—H22 | 120.1 |
| C4—C3—C2 | 119.6 (6) | C21—C22—H22 | 120.1 |
| C4—C3—H3 | 120.2 | C22—C23—C24 | 120.7 (6) |
| C2—C3—H3 | 120.2 | C22—C23—H23 | 119.6 |
| C5—C4—C3 | 121.4 (6) | C24—C23—H23 | 119.6 |

| | | | |
|---|---|---|---|
| C5—C4—H4 | 119.3 | C25—C24—C23 | 119.5 (6) |
| C3—C4—H4 | 119.3 | C25—C24—H24 | 120.2 |
| C4—C5—C6 | 119.9 (6) | C23—C24—H24 | 120.2 |
| C4—C5—H5 | 120.1 | C26—C25—C24 | 120.3 (6) |
| C6—C5—H5 | 120.1 | C26—C25—H25 | 119.8 |
| C7—C6—C5 | 118.4 (6) | C24—C25—H25 | 119.8 |
| C7—C6—H6 | 120.8 | C25—C26—C21 | 120.6 (6) |
| C5—C6—H6 | 120.8 | C25—C26—H26 | 119.7 |
| C2—C7—C6 | 122.1 (6) | C21—C26—H26 | 119.7 |
| C2—C7—H7 | 119.0 | Cl1<sup>ii</sup>—C27—Cl1 | 116.5 (11) |
| C6—C7—H7 | 119.0 | Cl1—C27—H27A | 108.2 |
| O1—C8—C9 | 108.1 (5) | Cl1<sup>ii</sup>—C27—H27A | 108.2 |
| O1—C8—H8A | 110.1 | Cl1—C27—H27B | 108.2 |
| C9—C8—H8A | 110.1 | Cl1<sup>ii</sup>—C27—H27B | 108.2 |
| O1—C8—H8B | 110.1 | H27A—C27—H27B | 107.3 |
| | | | |
| P1—Au—S1—C1 | 106.4 (6) | C11<sup>i</sup>—Fe—C12—C13 | 59.9 (5) |
| S1—Au—P1—C10 | 160.4 (6) | C11—Fe—C12—C13 | −120.1 (5) |
| S1—Au—P1—C21 | −76.2 (6) | C13<sup>i</sup>—Fe—C12—C13 | 180.000 (1) |
| S1—Au—P1—C15 | 39.7 (6) | C12<sup>i</sup>—Fe—C12—C13 | −49 (34) |
| C2—N1—C1—O1 | −177.6 (5) | C10—Fe—C12—C11 | 38.5 (3) |
| C2—N1—C1—S1 | 1.0 (9) | C10<sup>i</sup>—Fe—C12—C11 | −141.5 (3) |
| C8—O1—C1—N1 | −1.7 (8) | C14<sup>i</sup>—Fe—C12—C11 | −96.8 (3) |
| C8—O1—C1—S1 | 179.5 (5) | C14—Fe—C12—C11 | 83.2 (3) |
| Au—S1—C1—N1 | −149.8 (5) | C11<sup>i</sup>—Fe—C12—C11 | 180.0 |
| Au—S1—C1—O1 | 28.9 (5) | C13<sup>i</sup>—Fe—C12—C11 | −59.9 (5) |
| C1—N1—C2—C7 | 115.8 (7) | C13—Fe—C12—C11 | 120.1 (5) |
| C1—N1—C2—C3 | −70.2 (8) | C12<sup>i</sup>—Fe—C12—C11 | 71 (32) |
| C7—C2—C3—C4 | −1.5 (9) | C11—C12—C13—C14 | 0.9 (6) |
| N1—C2—C3—C4 | −175.5 (6) | Fe—C12—C13—C14 | 58.9 (4) |
| C2—C3—C4—C5 | 0.0 (10) | C11—C12—C13—Fe | −58.0 (4) |
| C3—C4—C5—C6 | 1.1 (10) | C10—Fe—C13—C14 | −38.5 (3) |
| C4—C5—C6—C7 | −0.6 (10) | C10<sup>i</sup>—Fe—C13—C14 | 141.5 (3) |
| N1—C2—C7—C6 | 176.1 (6) | C14<sup>i</sup>—Fe—C13—C14 | 180.0 |
| C3—C2—C7—C6 | 2.0 (9) | C11<sup>i</sup>—Fe—C13—C14 | 97.2 (4) |
| C5—C6—C7—C2 | −1.0 (10) | C11—Fe—C13—C14 | −82.8 (4) |
| C1—O1—C8—C9 | 173.2 (6) | C13<sup>i</sup>—Fe—C13—C14 | 54 (58) |
| C21—P1—C10—C11 | −160.4 (4) | C12—Fe—C13—C14 | −120.4 (5) |
| C15—P1—C10—C11 | 90.1 (5) | C12<sup>i</sup>—Fe—C13—C14 | 59.6 (5) |
| Au—P1—C10—C11 | −33.9 (5) | C10—Fe—C13—C12 | 81.9 (3) |
| C21—P1—C10—C14 | 22.0 (6) | C10<sup>i</sup>—Fe—C13—C12 | −98.1 (3) |
| C15—P1—C10—C14 | −87.4 (5) | C14<sup>i</sup>—Fe—C13—C12 | −59.6 (5) |
| Au—P1—C10—C14 | 148.5 (4) | C14—Fe—C13—C12 | 120.4 (5) |
| C21—P1—C10—Fe | −71.4 (4) | C11<sup>i</sup>—Fe—C13—C12 | −142.4 (3) |
| C15—P1—C10—Fe | 179.2 (3) | C11—Fe—C13—C12 | 37.6 (3) |
| Au—P1—C10—Fe | 55.1 (4) | C13<sup>i</sup>—Fe—C13—C12 | 174 (58) |

| | | | |
|---|---|---|---|
| C10[i]—Fe—C10—C11 | −160 (45) | C12[i]—Fe—C13—C12 | 180.000 (1) |
| C14[i]—Fe—C10—C11 | 61.1 (5) | C12—C13—C14—C10 | −0.5 (6) |
| C14—Fe—C10—C11 | −118.9 (5) | Fe—C13—C14—C10 | 59.1 (4) |
| C11[i]—Fe—C10—C11 | 180.0 | C12—C13—C14—Fe | −59.6 (4) |
| C13[i]—Fe—C10—C11 | 98.6 (4) | C11—C10—C14—C13 | −0.1 (6) |
| C13—Fe—C10—C11 | −81.4 (4) | P1—C10—C14—C13 | 177.8 (4) |
| C12—Fe—C10—C11 | −38.4 (4) | Fe—C10—C14—C13 | −60.0 (4) |
| C12[i]—Fe—C10—C11 | 141.6 (4) | C11—C10—C14—Fe | 59.9 (4) |
| C10[i]—Fe—C10—C14 | −41 (45) | P1—C10—C14—Fe | −122.2 (4) |
| C14[i]—Fe—C10—C14 | 180.0 | C10—Fe—C14—C13 | 118.7 (5) |
| C11[i]—Fe—C10—C14 | −61.1 (5) | C10[i]—Fe—C14—C13 | −61.3 (5) |
| C11—Fe—C10—C14 | 118.9 (5) | C14[i]—Fe—C14—C13 | −135 (100) |
| C13[i]—Fe—C10—C14 | −142.5 (3) | C11[i]—Fe—C14—C13 | −99.3 (4) |
| C13—Fe—C10—C14 | 37.5 (3) | C11—Fe—C14—C13 | 80.7 (4) |
| C12—Fe—C10—C14 | 80.5 (4) | C13[i]—Fe—C14—C13 | 180.0 |
| C12[i]—Fe—C10—C14 | −99.5 (4) | C12—Fe—C14—C13 | 36.7 (4) |
| C10[i]—Fe—C10—P1 | 83 (45) | C12[i]—Fe—C14—C13 | −143.3 (4) |
| C14[i]—Fe—C10—P1 | −55.7 (5) | C10[i]—Fe—C14—C10 | 180.0 |
| C14—Fe—C10—P1 | 124.3 (5) | C14[i]—Fe—C14—C10 | 106 (100) |
| C11[i]—Fe—C10—P1 | 63.2 (5) | C11[i]—Fe—C14—C10 | 142.0 (3) |
| C11—Fe—C10—P1 | −116.8 (5) | C11—Fe—C14—C10 | −38.0 (3) |
| C13[i]—Fe—C10—P1 | −18.3 (4) | C13[i]—Fe—C14—C10 | 61.3 (5) |
| C13—Fe—C10—P1 | 161.7 (4) | C13—Fe—C14—C10 | −118.7 (5) |
| C12—Fe—C10—P1 | −155.2 (4) | C12—Fe—C14—C10 | −82.1 (3) |
| C12[i]—Fe—C10—P1 | 24.8 (4) | C12[i]—Fe—C14—C10 | 97.9 (3) |
| C14—C10—C11—C12 | 0.6 (6) | C10—P1—C15—C16 | −2.2 (5) |
| P1—C10—C11—C12 | −177.4 (4) | C21—P1—C15—C16 | −114.1 (5) |
| Fe—C10—C11—C12 | 60.4 (4) | Au—P1—C15—C16 | 124.4 (4) |
| C14—C10—C11—Fe | −59.8 (4) | C10—P1—C15—C20 | −178.4 (4) |
| P1—C10—C11—Fe | 122.2 (4) | C21—P1—C15—C20 | 69.7 (5) |
| C10[i]—Fe—C11—C10 | 180.0 | Au—P1—C15—C20 | −51.9 (5) |
| C14[i]—Fe—C11—C10 | −141.8 (3) | C20—C15—C16—C17 | −1.2 (8) |
| C14—Fe—C11—C10 | 38.2 (3) | P1—C15—C16—C17 | −177.3 (4) |
| C11[i]—Fe—C11—C10 | 8(100) | C15—C16—C17—C18 | −0.1 (9) |
| C13[i]—Fe—C11—C10 | −98.6 (4) | C16—C17—C18—C19 | 0.8 (9) |
| C13—Fe—C11—C10 | 81.4 (4) | C17—C18—C19—C20 | −0.3 (10) |
| C12—Fe—C11—C10 | 118.1 (5) | C16—C15—C20—C19 | 1.7 (8) |
| C12[i]—Fe—C11—C10 | −61.9 (5) | P1—C15—C20—C19 | 178.1 (4) |
| C10—Fe—C11—C12 | −118.1 (5) | C18—C19—C20—C15 | −0.9 (9) |
| C10[i]—Fe—C11—C12 | 61.9 (5) | C10—P1—C21—C22 | −73.8 (5) |
| C14[i]—Fe—C11—C12 | 100.1 (4) | C15—P1—C21—C22 | 37.1 (5) |
| C14—Fe—C11—C12 | −79.9 (4) | Au—P1—C21—C22 | 157.9 (4) |
| C11[i]—Fe—C11—C12 | −110 (100) | C10—P1—C21—C26 | 108.5 (5) |

| | | | |
|---|---|---|---|
| C13[i]—Fe—C11—C12 | 143.3 (4) | C15—P1—C21—C26 | −140.7 (4) |
| C13—Fe—C11—C12 | −36.7 (4) | Au—P1—C21—C26 | −19.8 (5) |
| C12[i]—Fe—C11—C12 | 180.0 | C26—C21—C22—C23 | 0.2 (8) |
| C10—C11—C12—C13 | −0.9 (6) | P1—C21—C22—C23 | −177.6 (4) |
| Fe—C11—C12—C13 | 58.5 (4) | C21—C22—C23—C24 | 0.6 (9) |
| C10—C11—C12—Fe | −59.4 (4) | C22—C23—C24—C25 | −1.4 (9) |
| C10—Fe—C12—C13 | −81.5 (4) | C23—C24—C25—C26 | 1.5 (10) |
| C10[i]—Fe—C12—C13 | 98.5 (4) | C24—C25—C26—C21 | −0.7 (10) |
| C14[i]—Fe—C12—C13 | 143.1 (3) | C22—C21—C26—C25 | −0.1 (9) |
| C14—Fe—C12—C13 | −36.9 (3) | P1—C21—C26—C25 | 177.7 (5) |

Symmetry codes: (i) −$x$, −$y$, −$z$; (ii) −$x$, −$y$+1, −$z$+1.

*Hydrogen-bond geometry (Å, °)*

Cg1 and Cg2 are the centroids of the C2–C7 and C15–C20 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C9—H9a···Cg1[iii] | 0.97 | 2.75 | 3.623 (9) | 150 |
| C11—H11···Cg2[iv] | 0.94 | 2.78 | 3.619 (7) | 150 |

Symmetry codes: (iii) $x$−1, $y$, $z$; (iv) −$x$+1, −$y$, −$z$.

**Fig. 1**

**Fig. 2**