

Metallophilic interactions in iodido(2,2':6',2''-terpyridine)- platinum(II) diiodoaurate(I)

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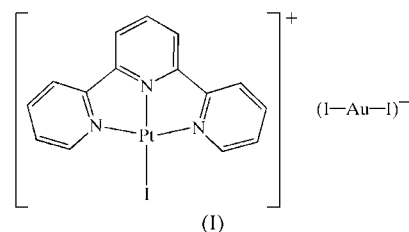
In the title compound, $[\text{Pt}(\text{C}_{15}\text{H}_{11}\text{N}_3)][\text{AuI}_2]$, the $[\text{Pt}(\text{terpy})]^+$ cations (terpy is 2,2':6',2''-terpyridine) stack in pairs about inversion centers through $\text{Pt}\cdots\text{Pt}$ interactions of 3.5279 (5) Å. The $[\text{AuI}_2]^-$ anions also exhibit pairwise stacking, with $\text{Au}\cdots\text{I}$ distances of 3.7713 (5) Å. The $[\text{Pt}(\text{terpy})]^+$ cations and $[\text{AuI}_2]^-$ anions aggregate forming infinite arrays of stacked $\cdots\{[\text{Pt}(\text{terpy})]^+\cdots[\text{Pt}(\text{terpy})]^+\}\cdots\{[\text{AuI}_2]^- \cdots [\text{AuI}_2]^- \}$ units.

Comment

Metallophilicity has been observed as a subtle yet significant force in forming $M\cdots M$ contacts (Pyykkö, 1997). We are interested in making wires of sub-millimeter length in single-crystal form with single-atom-wide conducting paths in the center and have synthesized double salts of $[\text{X-Pt-terpy}][\text{AuX}'_n]$, where terpy is 2,2':6',2''-terpyridine, X is CN or Cl, X' is a halogen and n is 2 or 4 (Hayoun *et al.*, 2006). The title compound, $[\text{Pt}(\text{terpy})][\text{AuI}_2]$ (I), is closely related to the reported $[\text{PtCl}(\text{terpy})][\text{AuCl}_2]$ double salt and, although the compounds differ only in the halide, this change has resulted in different crystal packing.

We report here the structure of (I); the asymmetric unit comprises a $[\text{Pt}(\text{terpy})]^+$ cation and an $[\text{AuI}_2]^-$ anion, as depicted in Fig. 1. A search of the Cambridge Structural Database (Version 5.28 of November 2006; Allen, 2002) for $[\text{PtX}(\text{terpy})]^+$ cations (X is any halogen) revealed the chloride derivative as the only structurally characterized form of the halogenated cation. The Pt atom in (I) is in a nearly square-planar environment, with an N1-Pt-N3 angle of 161.5 (2)°

and an N2-Pt-I1 angle of 176.68 (15)°. The Pt center lies 0.004 Å from the plane defined by the pyridine N atoms (N1, N2 and N3). The Pt1-I1 distance of 2.5930 (5) Å is comparable to the average $\text{Pt}^{\text{II}}-\text{I}$ distance of 2.62 (5) Å (Orpen *et al.*, 1994). The iodide ion lies 0.159 Å from the plane defined by the three N atoms, within the range of reported values seen in $[\text{PtCl}(\text{terpy})]^+$ cations, but above the average value of 0.05 (5) Å. The $[\text{Pt}(\text{terpy})]^+$ cations exhibit pairwise stacking with a symmetry-related cation, *viz.* $[\text{Pt}(\text{terpy})]^+$ at $(1-x, 1-y, 1-z)$, resulting in a $\text{Pt}\cdots\text{Pt}$ interaction of 3.5279 (5) Å. A weak hydrogen bond is present between the $[\text{Pt}(\text{terpy})]^+$ and $[\text{Pt}(\text{terpy})]^+$ cations [$\text{C15}\cdots\text{I1}^i = 3.824$ (7) Å and $\text{C15-H15A}\cdots\text{I1}^i = 140^\circ$; symmetry code: (i) $-x+2, -y+1, -z+1$], as depicted in Fig. 2.



The $[\text{AuI}_2]^-$ anion has been observed to undergo metallophilic interactions in compounds of the form $[\text{L}_2\text{Au}]^+[\text{AuI}_2]^-$. Two structurally characterized examples of $[\text{AuI}_2]^-$ -containing complexes exhibiting aurophilic interactions are the imidazolidine-2-thione derivative $[\text{Au}(\text{C}_3\text{H}_6\text{N}_2\text{S}_2)]^+[\text{AuI}_2]^-$ (Friedrichs & Jones, 1999) and $[\text{Au}(\text{tBuNC})_2]^+[\text{AuI}_2]^- (\text{I}_2)$ (Schneider *et al.*, 2005). Aurophilic interactions were also observed in the tetrahydrothiophene salt $[\text{Au}(\text{C}_4\text{H}_8\text{S}_2)]^+[\text{AuI}_2]^-$ (Ahrlund *et al.*, 1985) and the tetrahydrosephenone salt, $[\text{Au}(\text{C}_4\text{H}_8\text{Se}_2)]^+[\text{AuI}_2]^-$ (Ahrlund *et al.*, 1993). In (I), the nearly linear $[\text{AuI}_2]^-$ anion (Fig. 1) lies parallel to the *a* axis and exhibits an I2-Au1-I3 angle of 174.871 (17)°, consistent with previously reported values. The Au-I2 and Au1-I3 bond lengths of 2.5580 (5) and 2.5538 (5) Å, respectively, are also consistent with previously reported values. As shown in Fig. 2, the $[\text{AuI}_2]^-$ anions stack pairwise, with short contacts between atoms Au1 and I3 at $(-x+1, -y, -z)$, at a distance of 3.7713 (5) Å, about inversion centers.

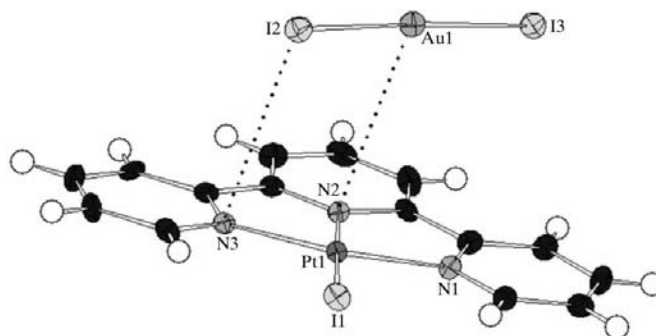
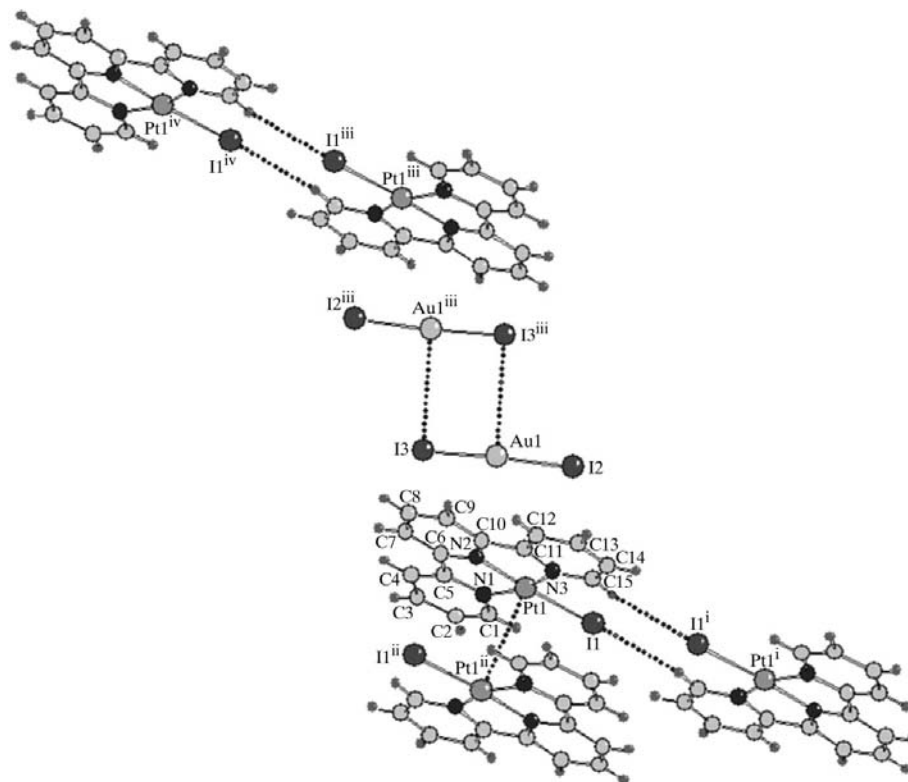
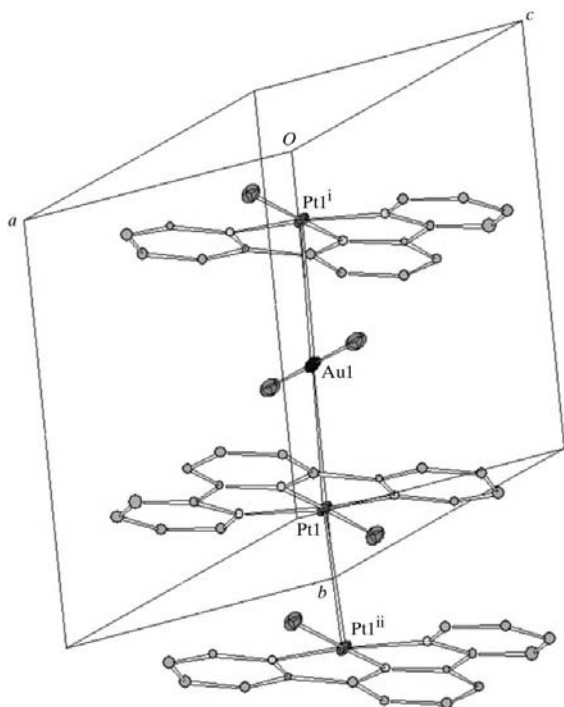


Figure 1

A view of the structure and stacking of the $[\text{Pt}(\text{terpy})]^+$ cation and $[\text{AuI}_2]^-$ anion. Closest contacts are joined with dotted lines. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.


Figure 2

A view of the stacking in the structure of (I). Close contacts and hydrogen bonds are shown as dotted lines. Selected distances: $\text{Au1} \cdots \text{I3}^{\text{iii}} = 3.7713$ (5) Å, $\text{Pt1} \cdots \text{Pt1}^{\text{ii}} = 3.5279$ (5) Å and $\text{C15} \cdots \text{I1}^{\text{i}} = 3.824$ (7) Å. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z$; (iv) $x - 1, y - 1, z - 1$.]


Figure 3

A view along the c axis of the $\{[\text{PtCl}(\text{terpy})]_2[\text{AuCl}_2]\}[\text{AuCl}_2]$ stacking, where the $[\text{AuCl}_2]^-$ anion without metallophilic interactions has been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x, -y + 2, -z$.]

In Fig. 1, the $[\text{AuI}_2]^-$ anions stack near the $[\text{PtI}(\text{terpy})]^+$ terpyridine planes, with atoms I2 and Au1 at distances of 3.667 and 3.571 Å, respectively, above the plane defined by the three terpyridine N atoms. The shortest contact between the $[\text{PtI}(\text{terpy})]^+$ cation and the $[\text{AuI}_2]^-$ anion is 3.629 (5) Å between atoms N2 and Au1 [a close contact between atoms N3 and I2 measures 3.727 (5) Å]. The shortest contact from the Pt atom in the cation to the anion is $\text{Pt1} \cdots \text{I2}$ of 3.9894 (5) Å [the $\text{Au1} \cdots \text{Pt1}$ distance is 4.2546 (4) Å; Fig. 2]. Although no continuous metal chain exists in (I), $\cdots[(\text{cation-cation}) \cdots (\text{anion-anion})] \cdots$ units are evident, and a pairwise metallophilic interaction exists between the Pt-containing cations.

The $[\text{Pt}^{\text{II}}\text{Cl}(\text{terpy})][\text{Cl}_2\text{Au}^{\text{I}}]$ derivative, which crystallizes to form red block-shaped crystals of $\{[\text{PtCl}(\text{terpy})]_2[\text{AuCl}_2]\}[\text{AuCl}_2]$, has been previously characterized (Hayoun *et al.*, 2006), and Fig. 3 shows the infinite metal chains consisting of $\cdots\text{Pt1} \cdots \text{Au1} \cdots \text{Pt1} \cdots \text{Pt1} \cdots$ contacts. An additional $[\text{AuCl}_2]^-$ anion is found perpendicular to the terpyridine planes. In the chlorido derivative, the $\text{Pt1} \cdots \text{Pt1}$ distance is 3.453 (1) Å and the $\text{Au1} \cdots \text{Pt1}$ contact is 3.268 (1) Å.

As iodine is less electronegative than chlorine, one would expect more electron density on the metal centers in (I) than in the Cl derivative; this is expected to promote metallophilic interactions in (I) (Ahrland *et al.*, 1993). Humphrey *et al.* (2004) prepared (isocyanide)gold(I) halides in which the extent of metallophilicity was shown to be dependent on the nature of the halide substituent. As the I atoms are larger than

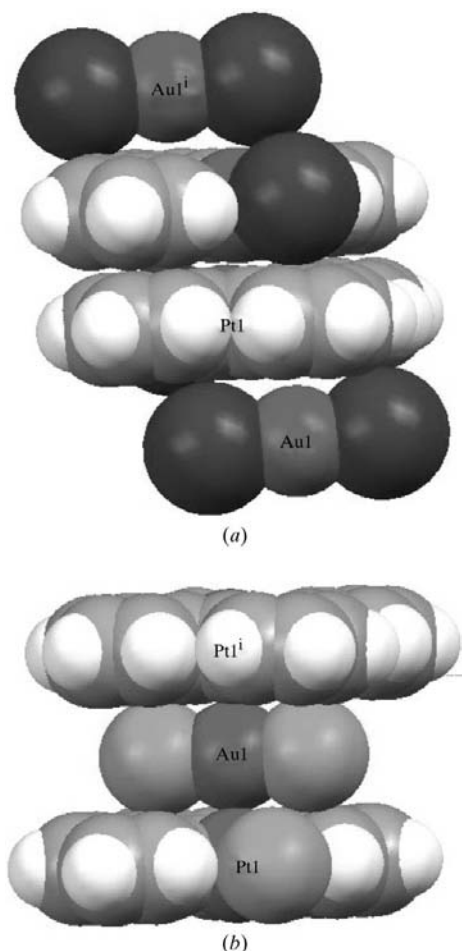


Figure 4
Space-filling diagrams (Mercury; Macrae *et al.*, 2006) of (a) compound (I) [symmetry code: (i) $1 - x, 1 - y, 1 - z$] and (b) $\{[\text{PtCl}(\text{terpy})]_2[\text{AuCl}_2]\}[\text{AuCl}_2]$, where the anion without metallophilic interactions has been omitted for clarity [symmetry code: (i) $-x, -y + 1, -z$].

the Au atom, the Au center in the $[\text{AuI}_2]^-$ anion is sterically hindered from metallophilically interacting with the Pt center, which is surrounded by a rigid planar ligand environment. Space-filling diagrams of (I) and the Cl derivative are shown in Figs. 4(a) and 4(b), respectively.

Synthesis of the bromido derivative of (I) is in progress. Recrystallization of (I) from solvents other than dimethylsulfoxide is also underway, as the Cl derivative crystallized with one acetonitrile solvent molecule and such packing may influence the metallophilic interactions.

Experimental

$[\text{PtCl}(\text{terpy})]\text{Cl}$ (Annibale *et al.*, 2004) and $(\text{Et}_4\text{N})[\text{AuBr}_2]$ (Braunstein & Clark, 1973) were prepared according to literature procedures. For the synthesis of $[\text{PtI}(\text{terpy})]\text{I}$, $[\text{PtCl}(\text{terpy})]\text{Cl}$ (0.0504 g) was dissolved in water (5 ml) and to this was added a 0.4196 g portion of KI dissolved in water (3 ml). A thick bright-fuschia precipitate formed, which faded to an apricot color after 10 min. The solution was left to stand overnight, resulting in a uniform dark-canary-yellow precipitate, which was filtered off and washed with cold water for an 85.8% yield. Analysis calculated for $\text{C}_{15}\text{H}_{11}\text{I}_2\text{N}_3\text{Pt}$: C 26.41, H 1.63, N 6.16%; found: C 26.54, H 1.58, N 6.21%. For the synthesis of

$(\text{Et}_4\text{N})[\text{AuI}_2]$, a 0.3312 g portion of $(\text{Et}_4\text{N})[\text{AuBr}_2]$ was dissolved in absolute ethanol (4 ml) and to this solution was added a 0.3473 g portion of $(\text{Et}_4\text{N})\text{I}$ dissolved in absolute ethanol (4 ml); the solution was heated to 313 K for 1 min and then left to cool to room temperature. Upon heating, the solution turned a clear brown color and several minutes after cooling a dark-brown precipitate formed in 68% yield. For the synthesis of $[\text{PtI}(\text{terpy})][\text{AuI}_2]$, a 0.0525 g portion of $(\text{Et}_4\text{N})[\text{AuI}_2]$ was dissolved in absolute ethanol (15 ml) to produce a clear light-brown solution. This was added to a partially dissolved solution of 0.0625 g of $[\text{PtI}(\text{terpy})]\text{I}$ in absolute ethanol (415 ml), which turned fuschia–orange and opaque and was stirred for 5 min to give a 83% yield of (I). X-ray quality crystals were grown from dimethyl sulfoxide and vapor diffused with diethyl ether.

Crystal data

$[\text{Pt}(\text{C}_{15}\text{H}_{11}\text{N}_3)][\text{AuI}_2]$	$\gamma = 87.554 (1)^\circ$
$M_r = 1006.02$	$V = 933.26 (11) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.7124 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.0668 (6) \text{ \AA}$	$\mu = 20.30 \text{ mm}^{-1}$
$c = 11.9860 (8) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 84.085 (1)^\circ$	$0.18 \times 0.13 \times 0.10 \text{ mm}$
$\beta = 82.476 (1)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	9589 measured reflections
Absorption correction: multi-scan (SADABS; Blessing, 1995; Sheldrick, 1996)	4155 independent reflections
$T_{\min} = 0.121, T_{\max} = 0.236$ (expected range = 0.067–0.131)	4099 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	208 parameters
$wR(F^2) = 0.065$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 1.43 \text{ e \AA}^{-3}$
4155 reflections	$\Delta\rho_{\text{min}} = -1.81 \text{ e \AA}^{-3}$

Data collection: SMART (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: CAMERON (Watkin *et al.*, 1996) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: publCIF (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3082). Services for accessing these data are described at the back of the journal.

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