Two polymorphs of chlorido(cyclo-hexyldiphenylphosphine)gold(I)

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The title compound, $[AuCl(C_{18}H_{21}P)]$, a monomeric two-coordinate gold(I) complex, has been characterized at 100 K as two distinct monoclinic polymorphs, one from a single crystal, (Is), and one from a pseudo-merohedrally twinned crystal, (It). The molecular structures in the two monoclinic [$P2_1/n$ for (Is) and $P2_1/c$ for (It)] polymorphs are similar; however, the packing arrangements in the two lattices differ considerably. The structure of (It) is pseudo-merohedrally twinned by a twofold rotation about the a* axis.

Comment

Recently, there has been a significant increase in the amount of research focused on the synthesis, characterization and theoretical analysis of gold clusters and nanoparticles, as their potential applications encompass ever-increasing areas of modern technology and scientific advances, ranging from biological luminophores to the components of plasmonic devices and catalysis. Their ability to guide, enhance, emit and modify optical fields puts them on the center stage for such applications as photonic crystals, biosensors and optical materials (Pyykkö, 2004, 2005; Andres *et al.*, 1996).


(I)
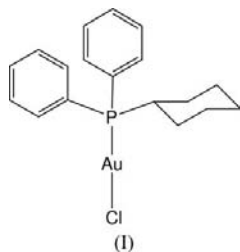
In our attempt to synthesize small luminescent gold clusters, we treated a preformed gold–phosphine cluster, $[Au_6(PPh_2-Cy)_6](NO_3)_2$ (Cy is cyclohexyl; Briant *et al.*, 1986), with either n-butylamine or i-propylamine in various ratios in acetonitrile. The process yielded an unstable luminescent gold-containing product, the crystallization of which from its CH_2Cl_2 solution by layering with pentane resulted in the reaction of this

luminescent gold species with CH_2Cl_2, yielding the title compound, (I), in high yield.

Compound (I) has been characterized at 100 K as two distinct monoclinic polymorphs, one from a single crystal, (Is), and one from a pseudo-merohedrally twinned crystal, (It). The structures of (Is) and (It) are shown in Figs. 1 and 2, and their overlap is shown in Fig. 3.

The space groups are $P2_1/n$ and $P2_1/c$ for (Is) and (It), respectively; both contain one molecule in the asymmetric unit. The nonconventional setting for (Is) was chosen based on the proximity of the β-angle value to 90°. A Cambridge Structural Database (CSD, September 2009 release; Allen, 2002) search revealed four other $P2_1/c$–$P2_1/c$ (or $P2_1/n$) monoclinic polymorphic pairs for phosphine–gold complexes: chloro(trimesitylphosphine)gold(I) in $P2_1/c$ (Alyea *et al.*, 1993) and $P2_1/c$ (Bott *et al.*, 2000), both at room temperature (RT); $[OPh_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]\cdot 4CH_2Cl_2$ in $P2_1/c$ and $P2_1/n$, both at 173 K (Fernandez *et al.*, 1993); [tris(2-cyanoethyl)phosphine]gold(I) in $P2_1/c$ and $P2_1/c$, both at RT (Fackler *et al.*, 1994); (tricyclohexylphosphine)gold(I) 2-mer-
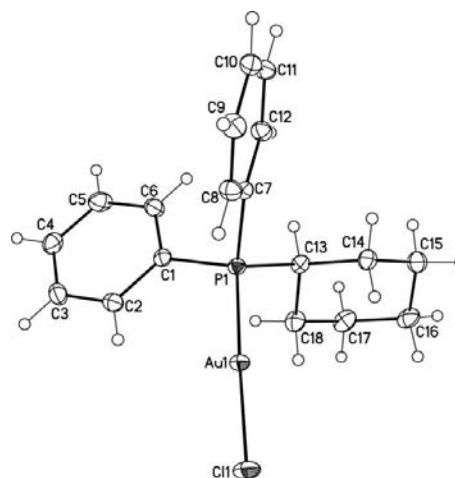
Figure 1
The molecular structure of (Is). Displacement ellipsoids are shown at the 50% probability level.
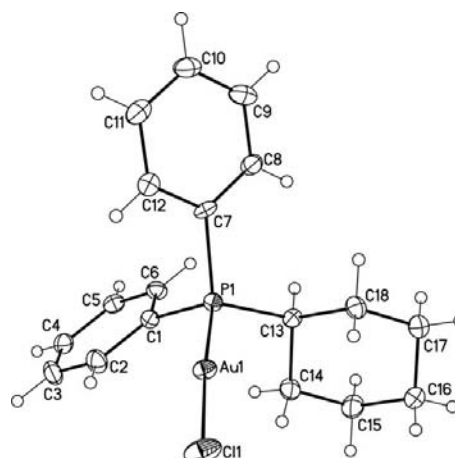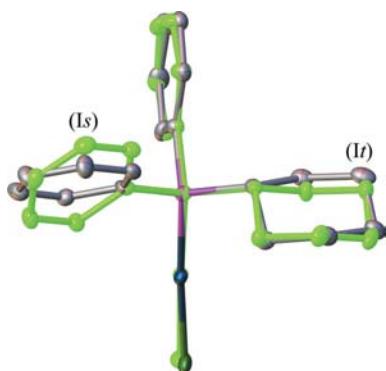

Figure 2
The molecular structure of (It). Displacement ellipsoids are shown at the 50% probability level.

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captobenzoate, with form I in $P\bar{1}$ at RT (Cookson & Tiekink, 1992), form II in $P2_1/n$ at 173 K, form III in $P2_1/n$ at 173 K, and form IV in $P\bar{1}$ at 173 K, all by Smyth *et al.* (2001).

There are no aurophilic interactions in either structure of (I). The overall packing is based on a ball motif, because the smallest box circumscribing the molecule is approximately isometric, measuring $10.51 \times 11.03 \times 10.98$ Å for (Is), and $10.56 \times 10.96 \times 11.86$ Å for (It). Interestingly, the volumes of these boxes, *viz.* 1272.0 Å^3 for (Is) and 1373.6 Å^3 for (It), differ by over 100 Å. Crystal packing in the two lattices is dissimilar (Fig. 4). The packing patterns were examined with a matching routine of the program *Mercury* (Bruno *et al.*, 2002), which was able to superimpose five molecules out of 20 from the two structures with an r.m.s. deviation of 0.843 Å. The theoretically computed powder patterns have a similarity value of 0.921. Thus, the two polymorphs are indeed distinct.

Unfortunately, it was not possible to establish which polymorph is more stable based on the crystals' density or melting-point measurements. The polymorph densities differ by only 0.005 Mg m^{-3}, and crystals of (Is) and (It) melted within 0.5 K of each other between 485 and 486 K. The unavailability of crystals of (It) did not allow for additional, possibly more conclusive, melting-point measurements. We did compare the theoretically computed energies corresponding to the observed molecular conformations in (Is) and (It). The geometries of the complexes were optimized with *GAUSSIAN03* (Frisch *et al.*, 2004) using the hybrid DFT PBE1PBE functional of TZVP triple-ζ quality with a polarization basis set on all nonmetallic atoms and the SDD basis set with a relativistically corrected Effective Core potential on gold. Our preliminary results suggest that (Is) is the more stable conformer, probably due to stronger Au$\cdots$H agostic interactions.

The molecular geometries of (Is) and (It) are typical, with bond distances and angles falling in the usual ranges. The P atom is in an equatorial position relative to the cyclohexyl ring. The two structures can be overlaid (Fig. 3), with an r.m.s. deviation of 0.323 Å computed based on all non-H atoms. Herein we compare the selected molecular parameters for (Is), (It), the molecular geometry of (I) optimized with *GAUSSIAN03*, (Ig), and the average parameters (based on 201 complexes in 154 crystal structures) for high-quality
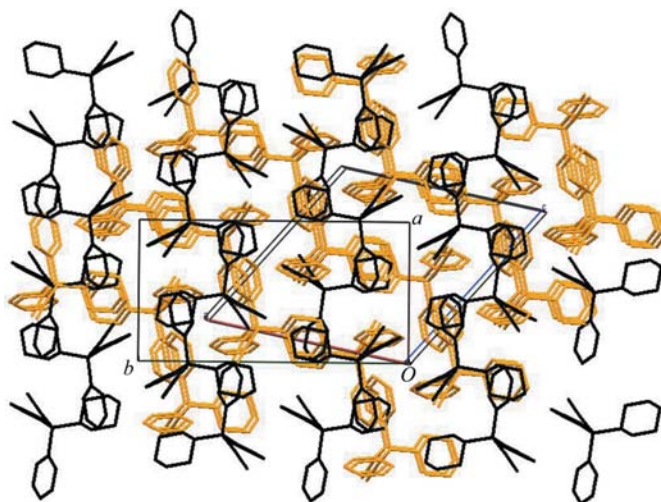
Figure 4
A partial overlay of the lattices of (Is) (black molecules) and (It) (lighter molecules; orange in the electronic version of the paper), viewed along the *c* axis of (Is). An attempt to overlay 15 molecules resulted in a more or less successful overlay of five molecules (best seen near the origin). The diagram contains more than 15 molecules to emphasize the differences in packing.

crystal structures of phosphine–gold complexes containing a Cl—Au—PC$_3$ unit as reported to the CSD, (II). The Au—Cl and Au—P bond distances and Cl—Au—P angle are 2.2885 (5), 2.2403 (5) Å and 177.668 (19)° in (Is), 2.2915 (14), 2.2335 (13) Å and 176.41 (5)° in (It), 2.2994, 2.2730 Å and 179.44° in (Ig), and 2.288 (11), 2.231 (10) Å and 176 (2)° for (II). The overall geometry of (Ig) compares well with that of (Is) and (It); however, the bond distances about the Au atom in (Ig) are slightly longer than in the experimentally established geometries. The results of the CSD search did not reveal any mutual dependence between the Au—Cl and Au—P bonds. Thus, the data probably indicate that the two polymorphs are 'conformational', and their existence is due to packing differences induced by different torsion angles, rather than by any change in covalent distances and angles.

The structure of (It) was pseudo-merohedrally twinned, likely due to the proximity of the β angle to 120° and similarity of the *a* and *c* axial lengths. We have recently reported a case of a nonmerohedrally twinned crystal of nonactin (Guzei *et al.*, 2009) and treated the twinning in (It) according to the procedure described therein. In the case of (It) the twin law (101 0$\bar{1}$0 00$\bar{1}$) corresponded to a 180° rotation about the *a** axis in reciprocal space. The contribution of the minor twin component was calculated to be 17.14 (9)%.

In summary, we have discovered and structurally characterized two polymorphs of a monomeric two-coordinate gold(I) complex Au(PPh$_2$Cy)Cl, one of which is pseudo-merohedrally twinned.

Figure 3
An overlay of structure (Is) (green in the electronic version of the paper) and (It).

Experimental

n-Butylamine (99.5%) were purchased from Aldrich. Ethanol, methanol, tetrahydrofuran, dichloromethane and pentane were purchased from Acros. Cyclohexyldiphenylphosphine (98%, PCyPPh$_2$)

was purchased from Strem chemicals. NaBH$_4$ (98%) was purchased from Alfa Aesar. All the chemicals were used as received without further purification. The [Au$_6$(PCyPh$_2$)$_6$](NO$_3$)$_2$ cluster was prepared by reduction of Au(PCyPh$_2$)NO$_3$ with NaBH$_4$ in ethanol, as described by Briant *et al.* (1986). [Au$_6$(PCyPh$_2$)$_6$](NO$_3$)$_2$ (0.0175 g) was dispersed in dichloromethane (10 ml) to form a transparent yellow–brown solution. *n*-Butylamine (0.05 ml) was added to the above solution and stirred at room temperature for 5–7 d. Over time, the yellow–brown color of the original [Au$_6$(PCyPh$_2$)$_6$](NO$_3$)$_2$ cluster gradually disappeared producing a luminescent pale-yellow solution. The resulting solution was centrifuged and the supernatant was isolated in a flask and the solvent removed under vacuum to yield a light-yellow–brown precipitate. The precipitate was washed with hexane (twice) to remove excess amine and was then crystallized from dichloromethane by slow diffusion of pentane into the solution. One crystallization batch produced (I*s*), whereas a repetition of the reaction and crystallization produced (I*t*).

Compound (I*s*)

Crystal data

[AuCl(C$_{18}$H$_{21}$P)]	$V = 1721.97$ (12) Å^3
$M_r = 500.73$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.0059$ (4) Å	$\mu = 8.78$ mm^{-1}
$b = 17.2762$ (7) Å	$T = 100$ K
$c = 11.0719$ (4) Å	$0.39 \times 0.36 \times 0.34$ mm
$\beta = 91.610$ (2)°	

Data collection

Bruker SMART APEXII area-detector diffractometer	28496 measured reflections
	5263 independent reflections
Absorption correction: analytical (*SADABS*; Bruker, 2009)	4832 reflections with $I > 2\sigma(I)$
$T_{min} = 0.131$, $T_{max} = 0.154$	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	190 parameters
$wR(F^2) = 0.037$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 1.13$ e Å^{-3}
5263 reflections	$\Delta\rho_{min} = -1.01$ e Å^{-3}

Compound (I*t*)

Crystal data

[AuCl(C$_{18}$H$_{21}$P)]	$V = 1717.8$ (2) Å^3
$M_r = 500.73$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.1440$ (9) Å	$\mu = 8.80$ mm^{-1}
$b = 11.4900$ (8) Å	$T = 100$ K
$c = 13.1056$ (9) Å	$0.33 \times 0.32 \times 0.27$ mm
$\beta = 119.786$ (2)°	

Data collection

Bruker SMART APEXII area-detector diffractometer	32548 measured reflections
	4184 independent reflections
Absorption correction: analytical (*SADABS*; Bruker, 2009)	4157 reflections with $I > 2\sigma(I)$
$T_{min} = 0.161$, $T_{max} = 0.197$	$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	191 parameters
$wR(F^2) = 0.088$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 2.20$ e Å^{-3}
4184 reflections	$\Delta\rho_{min} = -1.96$ e Å^{-3}

All H atoms were placed in idealized locations, with C—H distances of 0.95 Å for aromatic C atoms, 0.99 Å for secondary C atoms and 1.00 Å for the tertiary C atom, and refined as riding with U_{iso}(H) values set at $1.2U_{eq}$(C).

The outlier reflections were omitted based on the statistics test described in Prince & Nicholson (1983) and Rollett (1988), and implemented in the program *FCF_filter* (Guzei, 2007). The number of omitted outliers was 4 for (I*s*) and 47 for (I*t*).

For both compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* and *OLEX2* (Dolomanov *et al.*, 2009); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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