Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1995). *SHELXTL5*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sommerer, S. O., Westcott, B. L. & Abboud, K. A. (1994). *Acta Cryst.* C**50**, 48–50.
Sommerer, S. O., Westcott, B. L., Jircitano, A. J. & Abboud, K. A. (1995). *Inorg. Chim. Acta*, **238**, 149–153.
Timkovich, R. & Tulinsky, A. (1977). *Inorg. Chem.* **16**, 962–963.

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Cyano[tri(cyclohexyl)phosphino]gold(I), $[Au(CN)\{(C_6H_{11})_3P\}]$

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Abstract

A linear complex of gold(I) cyanide with tri(cyclohexyl)phosphine, $[Au(CN)(C_{18}H_{33}P)]$, has been synthesized and characterized by X-ray crystallographic analysis. Contrary to the ionic species formed with tris(2-cyanoethyl)phosphine, no ionic complex was formed in the case of tri(cyclohexyl)phosphine. The Au—C and Au—P distances of 2.006 (11) and 2.287 (3) Å, respectively, are similar to the corresponding distances in AuCN complexes of other tri(alkyl/aryl)phosphines.

Comment

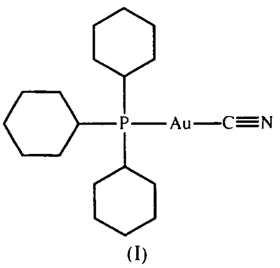
We recently reported the synthesis and solution equilibria (using NMR techniques) of a series of complexes of tri(alkyl/aryl)phosphines with gold(I) cyanide (Akhtar, Gazi, Isab, Al-Arfaj, Wazeer & Hussain, 1997). The X-ray structures revealed the formation of monomers as well as ionic complexes of these phosphines with gold(I) cyanide (Al-Arfaj, Hussain, Isab & Akhtar, 1996; Hussain, Al-Arfaj, Akhtar & Isab, 1996). The reaction of AuCN with tris(2-cyanoethyl)phosphine (CEP) resulted in the ionic complex $[(CEP)_2Au][Au(CN)_2]$, rather than the normally expected monomer [CEPAuCN] or trigonal $[(CEP)_2AuCN]$. The formation of the ionic species in solution was explained on the basis of ligand disproportionation [equation (2)] of the initially formed monomeric $[R_3PAuCN]$ complex [equation (1)],

$$2R_3P + AuCN \rightarrow [(R_3P)_2AuCN], \qquad (1)$$

$$2[(R_3P)_2AuCN] \rightarrow [(R_3P)_2Au][Au(CN)_2]. \qquad (2)$$

A combination of intrinsic factors such as steric (*e.g.* cone angles) and electronic characteristics of the phosphines, in addition to several extrinsic factors such as initial concentration of the complex and the nature of the counter-anions, are known to play an important role in determining the occurrence and extent of disproportionation. Although the large formation constant of $[Au(CN)_2]^-$ ($K = 4 \times 10^{28}$; Cotton & Wilkinson, 1972) tends to drive the ligand scrambling [equation (2)] in the forward direction, all $[R_3PAuCN]$ [R = methyl, isopropyl, cyclohexyl, *o*-tolyl, *m*-tolyl, *p*-tolyl, allyl, tricyanoethyl (CEP), 1-naphthyl and phenyl] complexes did not undergo the scrambling process. When R is cyclohexyl, the complex $[R_3PAuCN]$ takes several weeks in establishing the equilibrium in equation (2). This lack of formation of the ionic complex was explained on the basis of a much larger cone angle of 170° for the tri(cyclohexyl)phosphine (Hormann-Arendt & Shaw, 1990) compared with the cone angles of 118, 137 and 145° for the corresponding trimethyl-, triethyl-, and triphenylphosphines, respectively.

The ligand scrambling reactions of cyano–gold complexes are significant from a biological point of view. Administration of anti-arthritic gold drugs to smokers is known to produce a higher concentration of gold {in the form of $[Au(CN)_2]^-$} in their red blood cells, compared with non-smokers (Graham, Haavisto, Jones & Champion, 1984; Graham, Haavisto, McNaught, Browne & Champion, 1982; James, Ludvigsen, Cleland & Milazzo, 1982). Several recent studies have been directed towards the solution equilibria in R_2PAuCN complexes where $[Au(CN)_2]^-$, generated as a result of ligand scrambling, is believed to enter the red blood cells (Isab, 1992). The ^{13}C, ^{1}H, ^{15}N and/or ^{31}P NMR measurements in solution (Akhtar, Isab, Wazeer, Hussain & Al-Arfaj, 1996) could not differentiate between the monomers and the ionic species, prompting us to carry out the single-crystal structure determination of the title complex, (I).



(I)

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The Au atom in the title complex has asymmetric linear coordination (Fig. 1), with a P1—Au1—C1 angle of 177.0 (4)° (Table 1). The C1 atom of the CN^- ion is at 2.01 (1) Å from Au1, whereas P1 is at 2.287 (3) Å and has usual tetrahedral geometry. These distances are not significantly different from the corresponding distances in other tri(alkyl/aryl)phosphine complexes with AuCN. The corresponding Au—C and Au—P distances, respectively, are 1.85 (4) and 2.27 (4) Å in Ph_3PAuCN (Bellon, Manassero & Sansoni, 1969), 1.97 (2) and 2.288 (5) Å in Et_3PAuCN (Hormann, Shaw, Bennett & Reiff, 1986) and 2.00 (2), 2.06 (3) and 2.268 (6), 2.279 (6) Å in Me_3PAuCN (Ahrland, Aurivillius, Dreisch, Norén & Oskarsson, 1992). The three cyclohexyl groups are in chair configurations similar to those found in tri(cyclohexyl)phosphine sulfide (Reibenspies, Draper, Struck & Darensbourg, 1996) and the rings in the neighboring molecules stack on top of each other giving rise to a hole in the middle of the overall packing pattern. The Au···Au intermolecular distance is 7.698 (2) Å. Contrary to the ligand disproportionation observed in the case of [CEPAuCN] forming an ionic [$(CEP)_2Au$][$Au(CN)_2$] complex in liquid as well as in the solid state, the crystal structure of [$(cyclohexyl)_3PAuCN$] revealed no ligand scrambling, and only the monomeric species was observed in the crystalline form. Thus, the title complex is similar to [R_3PAuCN] (R = Me, Et and Ph) or to [CEPAuX] (X = Br^- or Cl^-), all of which have been crystallographically characterized as asymmetric linear monomeric species.

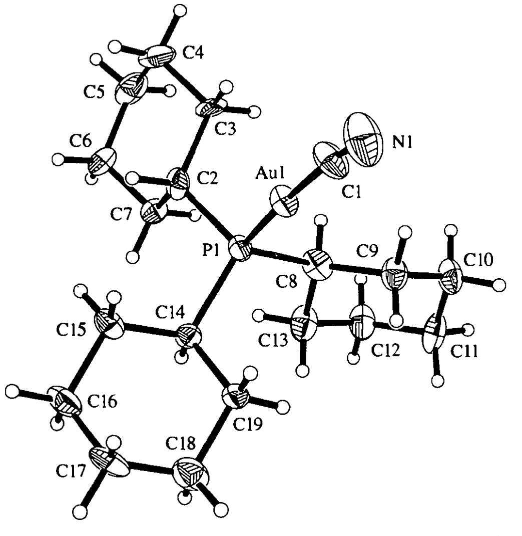

Fig. 1. View of cyano[tri(cyclohexyl)phosphino]gold(I), showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

Experimental

Firstly, [$(cyclohexyl)_3PAuCl$] was prepared by addition of the tricyclohexylphosphine to an ethanolic solution of $NaAuCl_4$ as reported earlier (Duddell, Goggin, Goodfellow, Norton & Smith, 1970). The title complex, [$(cyclohexyl)_3PAuCN$], was then synthesized by adding solid KCN directly to the ethanolic solution of [$(cyclohexyl)_3PAuCl$]. In another method, a slurry of Me_2SAuCl in acetone, and the phosphine ligand and KCN, both in the solid state, were mixed in the dark resulting in the title complex in approximately 75% yield.

Crystal data

[Au(CN)($C_{18}H_{33}P$)]
M_r = 503.40
Monoclinic
$P2_1/n$
a = 7.698 (2) Å
b = 16.647 (2) Å
c = 15.3084 (15) Å
β = 102.271 (12)°
V = 1916.9 (5) $Å^3$
Z = 4
D_x = 1.744 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 34 reflections
θ = 4.21–12.13°
μ = 7.756 mm^{-1}
T = 193 (2) K
Block
0.30 × 0.20 × 0.18 mm
Colorless

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (*XSCANS*; Siemens, 1994*b*)
T_{min} = 0.130, T_{max} = 0.248
3779 measured reflections
3374 independent reflections

2370 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -18 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.109
S = 1.018
3374 reflections
199 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.10 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.15 e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Au1—C1	2.006 (11)	P1—C2	1.833 (10)
Au1—P1	2.287 (3)	P1—C8	1.859 (10)
P1—C14	1.817 (9)	N1—C1	1.128 (13)
C1—Au1—P1	177.0 (4)	C8—P1—Au1	111.7 (3)
C14—P1—Au1	109.7 (3)	N1—C1—Au1	175.5 (12)
C2—P1—Au1	111.5 (3)		

A suitable crystal was chosen and mounted on a glass fiber at room temperature with epoxy cement. ω scans of several intense reflections indicated acceptable crystal quality. The 2θ-scan width was 2.0° + $K\alpha$ separation with a θ variable scan rate between 1.5 and 14.6° min^{-1}. Background measurement was by the stationary crystal and stationary counter technique at the beginning and end of each reflection for half the total scan time. Carbon-bound H atoms were placed in idealized positions [C—H = 0.96 Å and $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ of the adjacent C atom]. The H-atom parameters were not refined.

Data collection: *XSCANS* (Siemens, 1994*b*). Cell refinement: *XSCANS*. Data reduction: *XPREP* in *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*a*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1044). Services for accessing these data are described at the back of the journal.

References

Ahrland, S., Aurivillius, B., Dreisch, K., Norén, B. & Oskarsson, A. (1992). *Acta Chem. Scand.* **46**, 262–265.

Akhtar, M. N., Gazi, I. H., Isab, A. A., Al-Arfaj, A. R., Wazeer, M. I. M. & Hussain, M. S. (1997). *J. Coord. Chem.* **36**, 149–157.

Akhtar, M. N., Isab, A. A., Wazeer, M. I. M., Hussain, M. S. & Al-Arfaj, A. R. (1996). *J. Chem. Soc. Dalton Trans.* Accepted for publication.

Al-Arfaj, A. R., Hussain, M. S., Isab, A. A. & Akhtar, M. N. (1996). *Acta Cryst.* C**52**, 550–553.

Bellon, P. L., Manassero, M. & Sansoni, M. (1969). *La Riceus Sci.* **39**, 173–175.

Cotton, F. A. & Wilkinson, G. (1972). *Advanced Inorganic Chemistry*, 3rd ed., p. 1052. New York: John Wiley & Sons.

Duddell, D. A., Goggin, P. L., Goodfellow, R. J., Norton, M. G. & Smith, J. G. (1970). *J. Chem. Soc. A*, pp. 545–548.

Graham, G. G., Haavisto, T. M., Jones, H. M. & Champion, G. D. (1984). *Biochem. Pharmacol.* **33**, 1257–1262.

Graham, G. G., Haavisto, T. M., McNaught, P. J., Browne, C. D. & Champion, G. D. (1982). *J. Rheum.* **4**, 527–532.

Hormann, A. L., Shaw, C. F., Bennett, D. W. & Reiff, M. W. (1986). *Inorg. Chem.* **25**, 3953–3957.

Hormann-Arendt, A. L. & Shaw, C. F. III (1990). *Inorg. Chem.* **29**, 4683–4686.

Hussain, M. S., Al-Arfaj, A. R., Akhtar, M. N. & Isab, A. A. (1996). *Polyhedron*, **15**, 2781–2785.

Isab, A. A (1992). *J. Inorg. Biochem.* **45**, 145–150, and references therein.

James, D. W., Ludvigsen, N. W., Cleland, L. G. & Milazzo, S. C. (1982). *J. Rheum.* **9**, 532–537.

Reibenspies, J. H., Draper, J. D., Struck, G. & Darensbourg, D. J. (1996). *Z. Kristallogr.* **211**, 400–401.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994*a*). *XP. Interactive Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*b*). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Bis(*N*,*N*′-dimethylthiourea-*S*)gold(I) Perchlorate and Bis(*N*,*N*′-diethylthiourea-*S*)gold(I) Perchlorate

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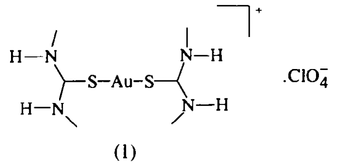
Abstract

The gold(I) center in each of the title complexes, $[\mathrm{Au(C_3H_8N_2S)_2}]\mathrm{ClO_4}$, (1), and $[\mathrm{Au(C_5H_{12}N_2S)_2}]\mathrm{ClO_4}$, (2), is essentially linearly coordinated through the S atoms of the dialkylthiourea ligands. The complexes crystallize in pairs, with an Au···Au separation of 3.620 (4) and 4.294 (2) Å for (1) and (2), respectively. The perchlorate anion does not interact with the bis(alkylthiourea)gold(I) cation. Compound (1) sits on a twofold axis.

Comment

Gold(I) complexes containing sulfur ligands are of interest as medicines (Parish & Cottrill, 1987) for the control of rheumatoid arthritis in cancer chemotherapy and also for their optical and electronic properties (Puddephatt, 1978). Thiourea ligands have long been used in the recovery of heavy metals from waste solutions. We have recently structurally characterized bis(thiourea)gold(I) bromide (Porter, Fackler, Costamagna & Schmidt, 1992). Continuing these Au—S structural studies, we have characterized bis(*N*,*N*′-dimethylthiourea)gold(I) perchlorate, (1), and bis(*N*,*N*′-diethylthiourea)gold(I) perchlorate, (2).



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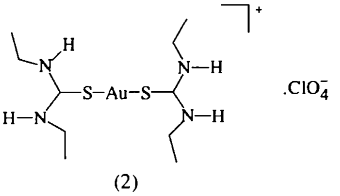

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