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Chlorobis(*N*,*N*′-di-2-pyridyl ketone oximato)gold(III) Hydrate

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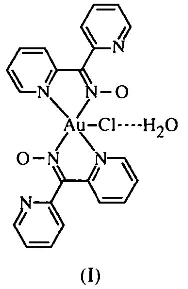
Abstract

Structural analysis of $[AuCl(C_{11}H_8N_3O)_2].H_2O$ revealed the Au atom to be in a square-pyramidal coordination environment with the $Au(C_{11}H_8N_3O)_2Cl$ moieties linked by hydrogen bonds to water molecules to form centrosymmetric dimers. The Au atom achieves a coordination number of five with four N atoms nearly coplanar and the fifth position occupied by a Cl atom.

Comment

The study of di-2-pyridyl ketone oxime (dpk-o) stems from its structural similarities to the di-2-pyridyl ketone (dpk) ligand (Sommerer, Westcott & Abboud, 1994) and its potential to bridge metals to form dimers and infinite chains (Sommerer, Westcott, Jircitano & Abboud, 1995).



(I)

The crystals of the title compound, (I), were found to consist of centrosymmetrically related $Au(dpk\text{-}o)_2Cl$ (Fig. 1) moieties linked by hydrogen bonds to water molecules to form dimers (Fig. 2). The Au atom achieves a coordination number of five with four N atoms nearly coplanar and the fifth position occupied by a Cl atom. The maximum deviation from the mean plane of the N atoms is 0.031 (2) Å and the Au atom is located 0.043 (2) Å below the plane. The geometry is clearly square pyramidal since there is no atom capable of coordination in a sixth position closer than 4.0 Å. The dimer is formed through hydrogen bonds between the chlorine and two separate water molecules, with Cl···O distances of 3.274 (6) and 3.461 (7) Å, respectively, for *OW*···Cl and *OW*···Cl^{i} [symmetry code: (i) $-x$, $1-y$, $-z$]. Each dpk-o ligand is deprotonated at the oxime function which together with the single chloride results in a neutral complex. Two observations provide evidence for the deprotonation of the dpk-o ligand: first, no electron-density peak

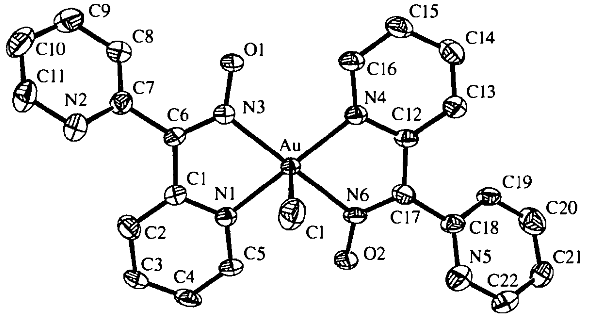


Fig. 1. Displacement ellipsoid drawing of the title compound with ellipsoids drawn at the 50% probability level.

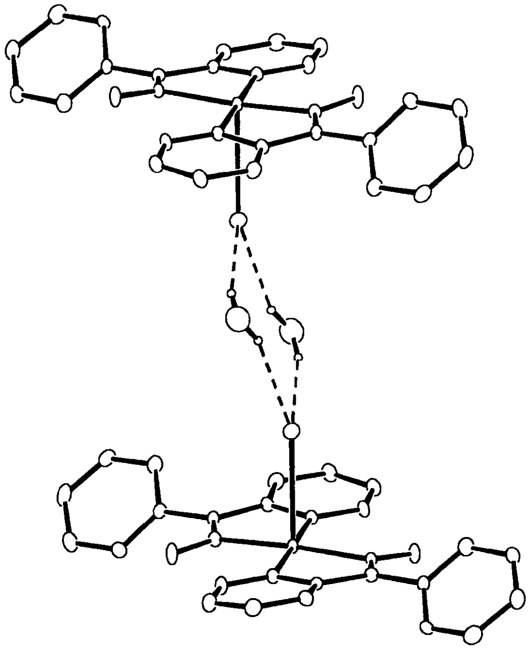


Fig. 2. Displacement ellipsoid drawing of the hydrogen-bonded dimer with the ellipsoids drawn at the 20% probability level.

corresponding to an oxime proton was observed in the final difference map; second, there is a pronounced shortening of both the N3—O1 and N6—O2 distances at 1.267 (5) and 1.263 (5) Å, respectively, compared with N—O distances of 1.393 (5) and 1.364 (4) Å reported previously (Sommerer, Westcott, Jircitano & Abboud, 1995) for related Ag(dpk-o) and Cu(dpk-o) complexes, where the presence of the oxime proton was clearly established.

Structures of five-coordinate gold(III) complexes are relatively rare. All are neutral and most have the composition Au(chelate)X_3, where 'chelate' represents a bidentate ligand and X is a halogen (Micklitz, Lippert, Müller, Mikulcik & Riede, 1989, and references therein). The exception is chloro(tetraphenylporphinato)gold(III) (Timkovich & Tulinsky, 1977), which is similar to Au(dpk-o)$_2$Cl in that a single chloride ion is in the axial position of a square pyramid and a dianionic ligand is in the square plane. Although five-coordinate intermediates have been proposed in ligand-exchange reactions of gold(III), the paucity of structures suggests an instability with respect to the square-planar starting materials. Complexes have only been isolated when an insoluble neutral product is formed.

Experimental

Di-2-pyridyl ketone oxime was combined with $KAuCl_4$ in a 2:1 stoichiometric ratio in 75 ml water at ambient temperature. Slow evaporation of the solvent at room temperature yielded crystals suitable for X-ray diffraction analysis.

Crystal data

$[AuCl(C_{11}H_8N_3O)_2].H_2O$
$M_r = 646.84$
Triclinic
$P\overline{1}$
$a = 9.368\ (2)$ Å
$b = 10.627\ (2)$ Å
$c = 12.219\ (2)$ Å
$\alpha = 76.67\ (3)°$
$\beta = 73.94\ (3)°$
$\gamma = 66.93\ (3)°$
$V = 1065.2\ (3)$ Å^3
$Z = 2$
$D_x = 2.017$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10–11°$
$\mu = 7.071$ mm^{-1}
$T = 298$ K
Tabular
0.25 × 0.21 × 0.11 mm
Red

Data collection

Siemens $P3m/V$ diffractometer
ω scans
Absorption correction: integration based on measured crystal faces (Sheldrick, 1995)
$T_{min} = 0.23$, $T_{max} = 0.46$
3744 measured reflections
3744 independent reflections

3348 reflections with $I > 2\sigma(I)$
$\theta_{max} = 24.99°$
$h = -10 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 14$
4 standard reflections every 96 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.027$
$wR(F^2) = 0.058$
$S = 1.085$
3744 reflections
298 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 2.2994P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.208$ e Å^{-3}
$\Delta\rho_{min} = -0.685$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Au—N1	2.037 (4)	N3—O1	1.267 (5)
Au—N4	2.044 (4)	N3—C6	1.316 (7)
Au—N3	2.073 (4)	N4—C16	1.333 (7)
Au—N6	2.095 (4)	N4—C12	1.363 (7)
Au—Cl	2.911 (2)	N5—C22	1.369 (8)
N1—C5	1.346 (6)	N5—C18	1.371 (7)
N1—C1	1.359 (7)	N6—O2	1.263 (5)
N2—C11	1.337 (7)	N6—C17	1.316 (7)
N2—C7	1.338 (7)		
N1—Au—N4	179.2 (2)	C22—N5—C18	117.1 (5)
N1—Au—N3	78.4 (2)	O2—N6—C17	123.9 (4)
N4—Au—N3	101.0 (2)	N1—C1—C2	119.4 (5)
N1—Au—N6	102.4 (2)	N1—C1—C6	115.2 (5)
N4—Au—N6	78.2 (2)	N3—C6—C1	114.9 (5)
N3—Au—N6	175.8 (2)	N3—C6—C7	121.5 (5)
N1—Au—Cl	85.33 (13)	N2—C7—C8	123.4 (5)
N4—Au—Cl	95.31 (13)	N2—C7—C6	116.2 (5)
N3—Au—Cl	91.51 (13)	N4—C12—C13	118.9 (5)
N6—Au—Cl	92.62 (13)	N4—C12—C17	115.2 (5)
C5—N1—C1	120.7 (5)	N6—C17—C12	115.3 (5)
C11—N2—C7	115.8 (5)	N6—C17—C18	122.7 (5)
O1—N3—C6	123.4 (4)	N5—C18—C17	119.0 (5)
C16—N4—C12	121.0 (5)		

During the refinement of the structure, no evidence of disorder between C and N atoms in the one uncoordinated pyridine (*i.e.* N2 and C8 or N5 and C19) was observed. Furthermore, the structure will not refine with the positions switched and there is no evidence of electron density near the N atom. Water H atoms were located from a difference synthesis; all other H atoms were included in calculated positions (C—H 0.93 Å). Displacement parameters were fixed at $1.2U_{iso}$ of bound carbon and $1.5U_{iso}$ of bound oxygen.

Data collection: *SHELXTL-Plus* (Sheldrick, 1991). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX5* (McArdle, 1995). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1030). Services for accessing these data are described at the back of the journal.

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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

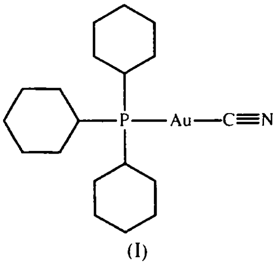
We recently reported the synthesis and solution equilibria (using NMR techniques) of a series of complexes of tri(alkyl/aryl)phosphines with gold(I) cyanide (Akhtar, Gazi, Isab, Al-Arfaj, Wazeer & Hussain, 1997). The X-ray structures revealed the formation of monomers as well as ionic complexes of these 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, ^1H, ^{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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