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#### 4:1 Lewis Base Adducts of Palladium Dichloride: [Pd(3-picoline)<sub>4</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O

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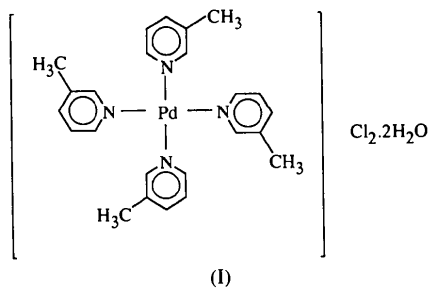
#### Abstract

The palladium ion of the title 4:1 Lewis base adduct, tetrakis(3-methylpyridine-*N*)palladium(II) dichloride dihydrate, [Pd(C<sub>6</sub>H<sub>7</sub>N)<sub>4</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O, is coordinated to four 3-methylpyridine ligands in a planar configuration with an average Pd—N distance of 2.024 (2) Å. Two chloride ions are in *trans* positions at a distance of 3.671 (2) Å from the palladium ion. The water molecules are each disordered over two sites with half occupancy.

#### Comment

Studies of palladium complexes in organic synthesis and catalytic processes, as well as studies of their chemical reactivity, spectroscopy and structural aspects have received great attention (Newkome *et al.*, 1985). Palladium(II) complexes possessing simple N-atom donors are well documented in the literature (Hartley, 1981) and a number of structural studies have been reported on these complexes. However, to the best of our knowledge, few examples of 4:1 Lewis base adducts of

palladium such as (4-ClC<sub>5</sub>H<sub>4</sub>N)<sub>4</sub>Pd(C<sub>5</sub>HF<sub>6</sub>O<sub>2</sub>)<sub>2</sub> have been characterized by single-crystal X-ray diffraction (Siedle & Pignolet, 1982). These palladium complexes were found to possess special uses in *ortho*-metallation (Siedle, 1981*a*), β-diketonate transfer reactions (Siedle, 1981*b*) and acid–base surface complexes formed by utilizing metal oxides as condensed-phase donor (Siedle, Sperl & Rusch, 1980; Siedle & Newmark, 1981). In this paper, we report the crystal structure of another 4:1 Lewis base adduct of palladium, namely, the 3-methylpyridine adduct [(3-picoline)<sub>4</sub>Pd]Cl<sub>2</sub>·2H<sub>2</sub>O, (I).



The geometry and the numbering scheme of the title compound is presented in Fig. 1. The Pd atom is coordinated to four picoline ligands in a square-planar arrangement and lies on a centre of symmetry. Weak contacts to two chloride ions, at distances of 3.671 (2) Å from the Pd atom, define the axial positions of a grossly tetragonally distorted octahedron. The angles subtended by the two chlorides to N1 and N2 are 91.7 (1) and 88.3 (1), and 91.2 (1) and 88.8 (1)°, respectively. Similar distortion is also ob-

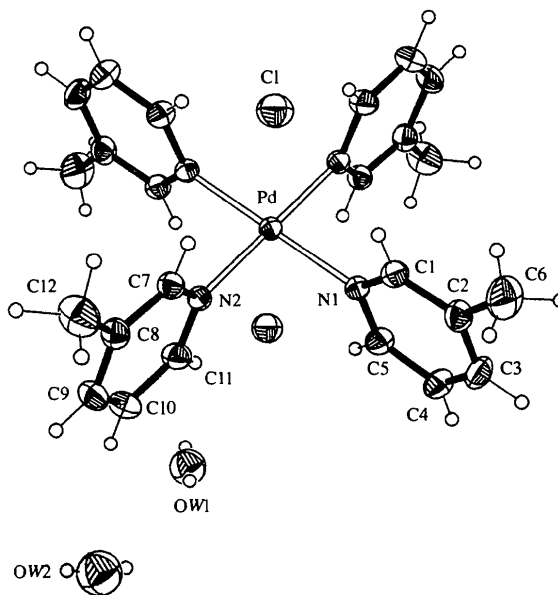


Fig. 1. ORTEP (Sheldrick, 1990*b*) plot drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.

served in  $(4\text{-ClC}_5\text{H}_4\text{N})_4\text{Pd}(\text{C}_5\text{HF}_6\text{O}_2)_2$  (Siedle & Pignolet, 1982). The Pd—N distances (average 2.025 Å) are in close agreement with other  $\text{PdN}_4$ -type complexes; 2.027 Å in  $(4\text{-ClC}_5\text{H}_4\text{N})_4\text{Pd}(\text{C}_5\text{HF}_6\text{O}_2)_2$  (Siedle & Pignolet, 1982), 2.038 Å in  $[(\text{bpy})_2\text{Pd}(\text{H}_2\text{O})_2](\text{NO}_3)_2$  (Siedle & Newmark, 1981), 2.036 Å in  $[\text{Pd}(\text{bpy})_2](\text{pic})_2$  (Maeda, Nishida, Okawa & Kida, 1986) and 2.025 Å in  $\text{Pd}(\text{trien})^{2+}$  (Hori, Matsumoto, Ooi & Kuroya, 1977).

As shown in Fig. 2, the Pd atom is located at the origin of the triclinic unit cell. Each  $\text{Cl}^-$  ion is hydrogen-bonded to four water molecules forming a zigzag chain parallel to the *a* axis between the planar cations. The  $\text{O}(\text{water}) \cdots \text{Cl}$  distances are 3.113 (8)–3.238 (8) Å. These parameters are comparable to those in other palladium(II) complexes *viz.*  $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ,  $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  and  $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (the separations are 3.1–3.3 Å between water and Cl, and 2.7–2.9 Å between water and water; Newkome, Frere, Fronczek & Gupta, 1985). Note, however, that the water sites are only half occupied (OW1 and its symmetry-related counterpart are too close to allow full occupancy).

The interplanar angle between the two asymmetric pyridyl rings is 86.96 (8)°.

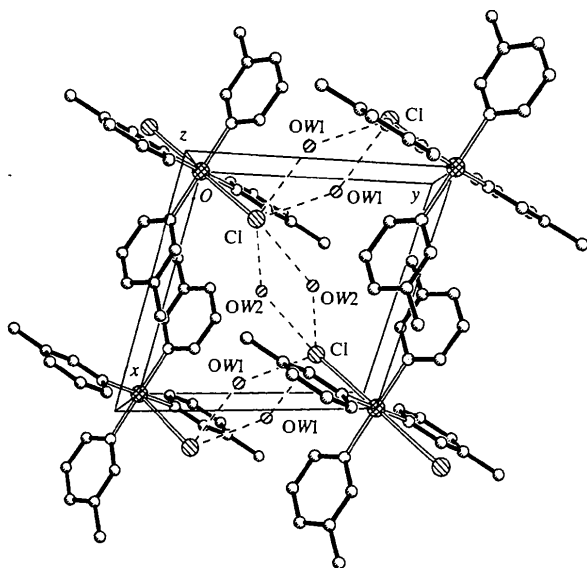


Fig. 2. Unit-cell packing diagram projected down the *c* axis.

## Experimental

The title complex was prepared by heating  $\text{PdCl}_2$  and 3-methylpyridine in the presence of dimercaptomethylene-propanedinitrilato-*S,S'*-dipotassium under reflux in ethanol for 2 h. The resulting solution was evaporated at room temperature for several days. Pale-yellow block-shaped crystals were obtained. The IR spectrum indicated the presence of crystal water (strong bands at 3462 and 3410  $\text{cm}^{-1}$ ).

## Crystal data

$[\text{Pd}(\text{C}_6\text{H}_7\text{N})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$   
 $M_r = 585.84$   
 Triclinic  
 $P\bar{1}$   
 $a = 9.070$  (1) Å  
 $b = 9.734$  (1) Å  
 $c = 9.779$  (2) Å  
 $\alpha = 117.86$  (1)°  
 $\beta = 112.16$  (1)°  
 $\gamma = 92.36$  (1)°  
 $V = 681.5$  (2) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.427$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 12\text{--}15^\circ$

$\mu = 0.903$  mm<sup>-1</sup>

$T = 300$  (2) K

Irregular

$0.5 \times 0.5 \times 0.4$  mm

Pale yellow

## Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega$ - $2\theta$  scans

Absorption correction:

$\psi$  scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.498$ ,  $T_{\max} = 0.697$

2561 measured reflections

2395 independent reflections

2358 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 24.97^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = 0 \rightarrow 11$

3 standard reflections

frequency: 60 min

intensity decay: none

## Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.083$

$S = 1.109$

2395 reflections

174 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.1347P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.943$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.634$  e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pd—N1	2.021 (2)	Pd—N2	2.026 (2)
N1—Pd—N2	90.71 (8)	N1'—Pd—N2	89.29 (8)
Symmetry code: (i) $-x, -y, -z$ .			

Site occupancies of 0.5 were assumed for the water molecules (for OW1, the symmetry equivalent sites must be mutually exclusive). H atoms on  $\text{CH}_3$  and  $\text{H}_2\text{O}$  were located from difference Fourier maps. The former were refined isotropically, while the latter were held fixed.

Data collection: *CAD-4 VAX/PC Operator's Manual* (Enraf-Nonius, 1988). Cell refinement: *CAD-4 VAX/PC Operator's Manual*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). 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: JZ1170). Services for accessing these data are described at the back of the journal.

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## A Linear Cluster with Mixed Ligands, [WCu<sub>2</sub>S<sub>4</sub>(tpt)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]

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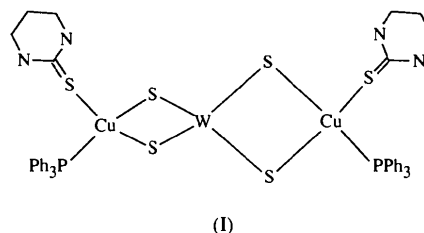
## Abstract

The structure determination of tetra- $\mu$ -sulfido-1:2 $\kappa^4$ S;-1:3 $\kappa^4$ S-bis(tetrahydropyrimidine-2-thione)-2 $\kappa$ S,3 $\kappa$ S-bis-(triphenylphosphine)-2 $\kappa$ P,3 $\kappa$ P-dicoppertungsten, [Cu<sub>2</sub>W-

S<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>S)<sub>2</sub>(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>], is reported. The compound contains a linear cluster core [CuS<sub>2</sub>WS<sub>2</sub>Cu]. Each Cu atom has a distorted tetrahedral coordination, from two S atoms of a tetradentate WS<sub>4</sub><sup>2-</sup> moiety, one S atom of tetrahydropyrimidine-2-thione (tpt) and one P atom of PPh<sub>3</sub>.

## Comment

Several linear clusters MS<sub>4</sub>M'(PPh<sub>3</sub>)<sub>3</sub>·0.8CH<sub>2</sub>Cl<sub>2</sub> (M = Mo, W; M' = Cu, Ag) have been prepared over the last two decades (Müller, Bögge & Schimanski, 1983). Additionally, the linear heterometallic trinuclear clusters [Et<sub>4</sub>N][(PPh<sub>3</sub>)<sub>2</sub>AgS<sub>2</sub>MS<sub>2</sub>Cu(CN)] (M = Mo, W) have been synthesized in recent years (Du, Zhu, Chen, Wu & Lu, 1992a,b). The title compound, (I), also has a linear core [CuS<sub>2</sub>W<sub>2</sub>Cu], but in which both Cu atoms are tetrahedrally coordinated by mixed ligands.



As shown in Fig. 1, the W atom has tetrahedral coordination, WS<sub>4</sub><sup>2-</sup>. Furthermore, each Cu atom is coordinated by a distorted tetrahedron of two S atoms of the tetradentate WS<sub>4</sub><sup>2-</sup> moiety, one S atom of tpt and one P atom of PPh<sub>3</sub>. The average W—Cu, W— $\mu$ -S and Cu— $\mu$ -S distances of 2.7525 (8), 2.201 (2) and 2.321 (2) Å, respectively, are comparable with the corresponding values of 2.740 (3), 2.214 (8) and 2.284 (8) Å found in (PPh<sub>3</sub>)<sub>3</sub>WS<sub>4</sub>Cu<sub>2</sub>·0.8CH<sub>2</sub>Cl<sub>2</sub>. The Cu—S<sub>tpt</sub> bond length of 2.363 (3) Å is longer than that of 2.206 (2) Å in [Cu(tpt)<sub>2</sub>Cl] (Bret, Castan & Jugie, 1983).

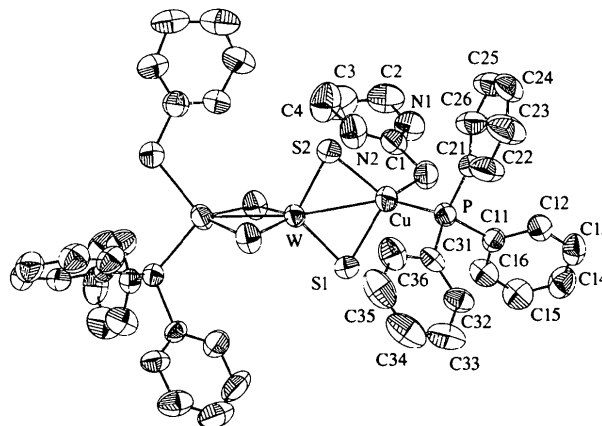


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.