$a = 8.9162\,(1)$ Å
$b = 9.6764\,(1)$ Å
$c = 20.0766\,(1)$ Å
$\alpha = 78.536\,(1)°$
$\beta = 81.520\,(1)°$
$\gamma = 83.922\,(1)°$
$V = 1673.79\,(3)$ Å$^3$
$Z = 2$
$D_x = 1.517$ Mg m$^{-3}$
$D_m$ not measured

$\mu = 0.624$ mm$^{-1}$
$T = 293\,(2)$ K
Parallelepiped
0.42 × 0.24 × 0.18 mm
Dark brown

*Data collection*

Siemens SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.780$, $T_{\max} = 0.896$
9910 measured reflections
6440 independent reflections

5610 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.014$
$\theta_{\max} = 26°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 24$
Intensity decay: negligible

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.207$
$S = 1.090$
6440 reflections
462 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1169P)^2 + 2.3590P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.250$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.804$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Mn1—O2 | 1.918 (3) | O2—C6 | 1.341 (5) |
| Mn1—O3 | 1.924 (3) | O3—C29 | 1.315 (5) |
| Mn1—N4 | 1.927 (4) | N4—C23 | 1.291 (6) |
| Mn1—N5 | 1.950 (4) | N5—C20 | 1.284 (6) |
| O2—Mn1—O3 | 90.19 (12) | O2—Mn1—N5 | 93.24 (14) |
| O2—Mn1—N4 | 176.59 (14) | O3—Mn1—N5 | 169.36 (15) |
| O3—Mn1—N4 | 93.13 (14) | N4—Mn1—N5 | 83.36 (16) |
| O3—Mn1—O2—C6 | 172.1 (3) | O2—Mn1—O3—C29 | 171.9 (3) |
| N4—Mn1—O2—C6 | −20 (3) | N4—Mn1—O3—C29 | −7.4 (3) |
| N5—Mn1—O2—C6 | −18.0 (3) | N5—Mn1—O3—C29 | 62.9 (9) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N32—H32···O1*W* | 0.91 | 2.01 | 2.782 (6) | 141 |
| N14—H14···O2 | 0.91 | 2.15 | 2.818 (4) | 129 |
| C33—H33*B*···O17$^{\text{i}}$ | 0.97 | 2.47 | 3.130 (6) | 125 |

Symmetry code: (i) $1 + x, y, z$.

Most of the H atoms were fixed geometrically. The remainder (H10, H18*A*, H18*B*, H20, H25, H31*A* and H31*B*) were located from difference Fourier maps and refined. The H atoms of the water molecule were not located.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1412). Services for accessing these data are described at the back of the journal.

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# Dichloro(ethylenediaminetetraacetic acid)-palladium(II) hexahydrate

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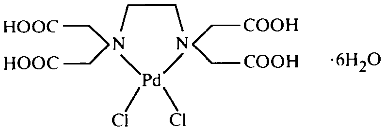
## Abstract

In the title compound, $[PdCl_2(C_{10}H_{16}N_2O_8)]\cdot 6H_2O$, the Pd$^{\text{II}}$ atom has a square-planar environment made up of two chloride anions and the two N atoms of ethylenediaminetetraacetic acid (edta), with the four carboxylic

acid moieties uncoordinated. The Pd—N and Pd—Cl distances are 2.087 (2) and 2.299 (1) Å, respectively, and the N—Pd—Cl angle is 91.7 (1)°. The molecule lies on a crystallographic twofold axis. The crystal structure is stabilized by an extensive array of hydrogen bonds involving the carboxylic acid groups and the water molecules.

## Comment

The study of the $Pd^{II}$ complex with ethylenediaminetetraacetic acid (edta), (I), was initiated for two reasons. Firstly, as a promoter of the cleavage of peptides, this complex was found to form a hydrolytically active mononuclear $Pd^{II}$ complex with the substrates which may be associated with proteins cleavage (Chen *et al.*, 1998). Secondly, although the crystal structure of the title complex was determined by Robinson & Kennard (1967) using Cu $K\alpha$ radiation (nickel-filtered, single-crystal oscillation and Weissenberg photographs), there are some shortcomings, *i.e.* the crystal data were incomplete, the space group was not unambiguously determined and a high $R$ value of 0.12 was obtained. We report here the detailed crystal structure data of the complex, with a low $R$ value of 0.032.



(I)

The edta molecule coordinates to the $Pd^{II}$ atom by chelating through the two N atoms to form a five-membered ring, while the four carboxylic acid groups are uncoordinated. The other two coordinating ligands are chloride anions, resulting in a square-planar coordination for $Pd^{II}$. The bond distances between $Pd^{II}$ and the ligand atoms are normal. The distances within the edta moiety are typical and are comparable with literature values (Robinson & Kennard, 1967, 1970). There is a $C_2$ axis along $Pd^{II}$ and the midpoint of the C5—C5$^{i}$ bond [symmetry code: (i) $-y, -x, \frac{3}{2}-z$], and the Pd atom thus lies in the least-squares plane through the four coordinated atoms (N1, N1$^{i}$, Cl1 and Cl$^{i}$). Both the Pd and Pt complexes (Robinson & Kennard, 1967, 1970; Busch & Bailar, 1956) have been reported to contain five water molecules, though the hydrogen-bonding distances in the present complex with six water molecules are all reasonable. There are, however, pronounced differences between the C=O and C—OH distances compared with the Pd analog (Whalen *et al.*, 1996). Molecules are held together by hydrogen bonds involving the H atoms bound to non-C atoms and those of the water molecules (Table 2).

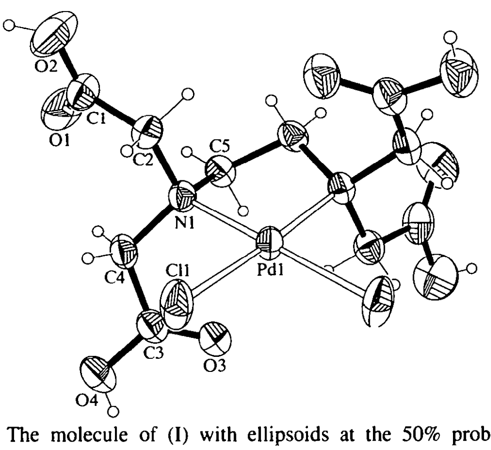


Fig. 1. The molecule of (I) with ellipsoids at the 50% probability level.

## Experimental

The title compound was prepared according to a published procedure (Busch & Bailar, 1956). To a solution of disodium dihydrogen edta (0.201 g, 0.54 mmol) was added $K_2PdCl_4$ (0.176 g, 0.54 mmol), after which the mixture was heated at about 353 K and stirred for 30 min. The resulting solution was cooled and concentrated HCl was added whereupon crystallization occurred. The product was filtered, washed twice with double-distilled water and dried in a vacuum. The product was then dissolved in double-distilled water and a few µl of HCl were added. The solution was evaporated at room temperature and orange single crystals were collected for crystallographic analysis.

*Crystal data*

$[PdCl_2(C_{10}H_{16}N_2O_8)]\cdot 6H_2O$
$M_r = 577.64$
Tetragonal
$P4_12_12$
$a = 10.1962$ (2) Å
$c = 21.0571$ (7) Å
$V = 2189.15$ (9) Å$^3$
$Z = 4$
$D_x = 1.753$ Mg m$^{-3$}
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6893 reflections
$\theta = 1.4$–33.2°
$\mu = 1.159$ mm$^{-1}$
$T = 293$ (2) K
Block
0.36 × 0.24 × 0.22 mm
Orange

*Data collection*

Siemens SMART CCD area-detector diffractometer
$\omega$ scan
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.667$, $T_{\max} = 0.775$
16 670 measured reflections
2473 independent reflections (plus 1707 Friedel-related reflections)

3795 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 33.35°$
$h = -15 \rightarrow 12$
$k = -8 \rightarrow 15$
$l = -32 \rightarrow 26$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.788$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.522$ e Å$^{-3}$

$S = 1.085$
4180 reflections
132 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.7536P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (4)

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

| | | | |
|---|---|---|---|
| Pd1—N1 | 2.0872 (19) | O2—C1 | 1.304 (4) |
| Pd1—Cl1 | 2.2991 (6) | O3—C3 | 1.213 (4) |
| N1—C2 | 1.484 (3) | O4—C3 | 1.310 (3) |
| N1—C4 | 1.485 (3) | C1—C2 | 1.523 (4) |
| N1—C5 | 1.498 (3) | C3—C4 | 1.500 (4) |
| O1—C1 | 1.190 (4) | | |
| N1—Pd1—Cl1 | 91.70 (6) | C2—N1—Pd1 | 105.60 (14) |
| C2—N1—C4 | 109.47 (19) | C4—N1—Pd1 | 112.74 (15) |
| C2—N1—C5 | 112.77 (19) | C5—N1—Pd1 | 105.91 (14) |
| C4—N1—C5 | 110.3 (2) | | |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O4—H4*C*···O2*W* | 0.82 | 1.79 | 2.602 (5) | 170 |
| O1*W*—H2*W*1···Cl1 | 1.03 | 2.23 | 3.133 (4) | 146 |
| O3*W*—H2O3···O1 | 0.86 | 2.15 | 2.858 (6) | 139 |
| O2—H2*C*···O1*W*$^{i}$ | 0.82 | 1.83 | 2.646 (6) | 176 |
| O2*W*—H2*W*2···O3*W*$^{ii}$ | 1.09 | 2.55 | 3.539 (8) | 151 |
| O2*W*—H1*W*2···O2*W*$^{iii}$ | 0.86 | 2.63 | 3.338 (7) | 140 |

Symmetry codes: (i) $x-1, y, z$; (ii) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$; (iii) $1-y, 1-x, \frac{1}{2}-z$.

H atoms on oxygen were located from difference maps, while those on carbon were placed in calculated positions, with C—H distances of 0.97 Å. $U_{\rm iso}$ values for the H atoms on C2 and C4 were assigned as $1.2U_{\rm eq}$ of the C atom, while those on C5 and the O atoms were assigned as $1.5U_{\rm eq}$ of the attached atom. H atoms were not refined.

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SAINT* (Siemens, 1996*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1173). Services for accessing these data are described at the back of the journal.

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# {4,4′-Dimethyl-6′-morpholiniomethyl-6-morpholinomethyl-2,2′-[1,2-ethanediylbis(iminomethylene)]diphenolato}copper(II) perchlorate dihydrate

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## Abstract

In the title compound, [$Cu(C_{28}H_{41}N_4O_4)$]$ClO_4$·$2H_2O$, the copper ion is in a square-pyramidal environment, with the basal plane being defined by the two phenoxy O and the two amino N atoms. Both morpholino rings are in chair conformations. The molecules are packed in the crystal with a three-dimensional hydrogen-bonding network involving the water molecules and the perchlorate ion.

## Comment

The study of metal complexes is focused very much towards the field of biomimicry where they can be used as model compounds for biological metallo compounds like proteins and enzymes (Suzuki *et al.*, 1984).

In the title complex, (I), the copper ion is coordinated by two phenoxy O and two amine N atoms in a

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