1985) to a solution obtained by treating Co(en)$_3$Cl$_3$ with CH$_2$O and NH$_3$ (Creaser *et al.*, 1982). The data for the cell determination revealed no evidence of twinning. The data were corrected for Lorentz and polarization effects. All non-H atoms were located through Patterson and Fourier techniques. Three H atoms were located by successive least-squares refinements associated with ΔF calculations and the remaining two, H11 and H12, were introduced in idealized positions. An empirical correction for absorption effects was applied (*ABSORB*; Ugozzoli, 1987, following Walker & Stuart, 1983) after the last isotropic refinement ($T_{\min}$ = 0.8998, $T_{\max}$ = 1.1708). Anisotropic thermal parameters were refined for all non-H atoms; H atoms were refined isotropically and held in fixed positions during the last cycles of refinement. Refinements performed with independent data collected using two further different crystals gave comparable results.

Complex (II) was prepared by treating (I) with concentrated HCl and an excess of NaNO$_3$; the resulting Co(sep)(NO$_3$)$_3$ was dissolved and then eluted on an anionic Cl$^-$ resin giving a solution from which crystals separated after slow evaporation. An empirical absorption correction was performed using three standard reflections. The data were corrected for Lorentz and polarization effects. Patterson interactions revealed the presence of two independent Co atoms; successive least-squares refinements and ΔF calculations enabled the remaining non-H and H atoms to be located. An empirical absorption correction (Walker & Stuart, 1983; Ugozzoli, 1987) was applied after the last isotropic refinement ($T_{\min}$ = 0.8986, $T_{\max}$ = 1.0654). Thermal parameters were refined anisotropically for non-H atoms and isotropically for H atoms; the H atoms were held fixed during the final least-squares cycles.

*SHELX*86 (Sheldrick, 1986) and *SHELX*76 (Sheldrick, 1976) were used for structure solution and refinement and *PARST* (Nardelli, 1983) for geometric calculations. *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1976) were used to produce the drawings. Extensive use was made of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). Calculations were performed on ENCORE-GOULD-POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55841 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1026]

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Structure of Di-μ-chloro-bis[bis(triphenylphosphine)palladium(II)] Bis(tetrafluoroborate) Acetone Solvate Dihydrate

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Abstract

The structure consists of a palladium dimer with bridging Cl atoms, two tetrafluoroborate anions and two water molecules and one acetone molecule. Each Pd atom in the dimer is surrounded by two Cl and two P atoms, forming a slightly distorted *cis* square-planar configuration.

Comment

Recently we have been using bridged dimers of Pd^{II} as catalysts in homogeneously catalyzed alkene hydration reactions (Ganguly & Roundhill, 1991). During the course of this research we became interested in certain structural features of these bridged dimers such as their intermetallic distances and their dihedral angles between the coordination planes of the Pd centers. Since there have been relatively few structural studies of chloro-bridged dimers of Pd^{II}, we have solved the structure of the title compound.

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The cation has a crystallographically imposed C_2 symmetry with the two Cl atoms, as well as the central C and the O atoms of the solvent acetone, lying on the twofold axis. The square-planar configuration around the metal atom in the dimer is slightly distorted with angle Cl(1)—Pd—P(2) of 175.7 (1)° and angle Cl(2)—Pd—P(1) of 172.05 (9)°. The Cl(1)—Pd—Cl(2) angle of 84.89 (9)° is significantly acute. The angles Cl(1)—Pd—P(1) and Cl(2)—Pd—P(2) at 89.40 (9) and 90.8 (1)° are close to right angles. The maximum deviation from the weighted least-squares plane is 0.104 (2) Å for the P(1) atom, and the maximum deviating angle is 94.86 (9)° for the P(1)—Pd—P(2) angle. The dihedral angle between the two coordination planes is only 3.8 (2)°, which is close to the reported value of 1.30 (7)° found in the complex [Pd(μ-Cl)(NO_2)(P^nPr_3)]$_2$ (Bruno, Campagna, Cusumano, Gianetto & Ricevuto, 1989). The Pd—Cl bond distances of 2.386 (3) and 2.354 (3) Å are similar to those found in other dichloro-bridged Pd dimers (Nifant'ev, Kukhareva, Antipin, Struchkov & Klabunovsky, 1983; Berry, Beveridge, Bushnell & Dixon, 1985). The Pd—P bond lengths of 2.290 (2) and 2.256 (2) Å are also within the expected range that is characteristic for tertiary phosphine coordination in square-planar Pd^{II} complexes.

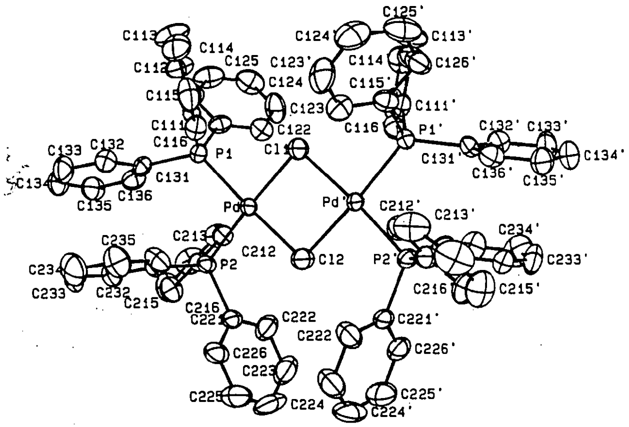

Fig. 1. Molecular structure and labeling scheme of the title complex. Thermal ellipsoids are drawn at the 30% probability level.

Experimental

Crystal data

$[Pd_2Cl_2\{P(C_6H_5)_3\}_4](BF_4)_2$
M_r = 1600.58
Monoclinic
$C2/c$
a = 18.414 (2) Å
b = 16.938 (2) Å
c = 22.577 (2) Å
β = 96.966 (7)°
V = 6990 (1) Å^3
Z = 4
D_x = 1.519 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12-16.67°
μ = 0.7420 mm^{-1}
T = 291 K
Prismatic
0.53 × 0.43 × 0.43 mm
Yellow
Crystal source: slow evaporation of acetone solution

Data collection

CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.734, T_{max} = 1.287
6349 measured reflections
6143 independent reflections
4576 observed reflections [$I \geq 3\sigma(I)$]

R_{int} = 0.028
θ_{max} = 25.00°
h = 0 → 21
k = 0 → 20
l = −26 → 26
3 standard reflections
frequency: 180 min
intensity variation: 5.9% total loss for 63.7 h experiment

Refinement

Refinement on F
Final R = 0.067
wR = 0.081
S = 1.452
4576 reflections
388 parameters
H-atom parameters not refined
$4F^2/[\sigma^2(I)+(0.04F^2)^2]$

$(\Delta/\sigma)_{max}$ = 0.15
$\Delta\rho_{max}$ = 1.226 e Å^{-3}
$\Delta\rho_{min}$ = −0.341 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: CAD-4 Version 5.0 (Schagen, Staver, van Meurs & Williams, 1989). Cell refinement: CAD-4 Version 5.0. Program(s) used to solve structure: *MolEN* (Enraf-Nonius, 1990). Program(s) used to refine structure: *MolEN*; *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. The B and F atoms were refined isotropically.

	x	y	z	B_{eq}
Pd	0.01035 (4)	0.23763 (4)	0.17401 (3)	2.21 (1)
Cl1	0.000	0.3335 (2)	0.250	3.49 (7)
Cl2	0.000	0.1446 (2)	0.250	4.87 (9)
P1	0.0075 (1)	0.3372 (1)	0.1052 (1)	2.39 (4)
P2	0.0198 (1)	0.1400 (1)	0.1074 (1)	2.51 (5)
F1	0.261	0.193	0.336	22.2
F2	0.274	0.278	0.258	19.2
F3	0.161	0.222	0.267	19.2
F4	0.255	0.145	0.240	19.2
O1	0.500	0.1787 (9)	0.250	8.3 (4)
O2	0.3711 (7)	0.2577 (9)	0.1816 (6)	11.2 (4)
C1	0.500	0.109 (1)	0.250	5.5 (4)
C2	0.436	0.063 (1)	0.268	7.2 (4)
C111	−0.0681 (5)	0.4014 (5)	0.1183 (4)	2.6 (2)
C112	−0.0679 (6)	0.4810 (6)	0.1031 (5)	4.3 (2)
C113	−0.1269 (7)	0.5277 (7)	0.1115 (6)	5.5 (3)
C114	−0.1861 (6)	0.4956 (7)	0.1343 (5)	4.7 (3)
C115	−0.1881 (6)	0.4179 (8)	0.1481 (5)	4.4 (3)
C116	−0.1282 (5)	0.3701 (6)	0.1398 (4)	3.4 (2)
C121	0.0927 (5)	0.3941 (5)	0.1161 (4)	3.0 (2)
C122	0.1409 (5)	0.3839 (6)	0.1665 (5)	3.6 (2)
C123	0.2038 (6)	0.4283 (8)	0.1748 (5)	5.0 (3)
C124	0.2198 (6)	0.4830 (7)	0.1332 (6)	5.3 (3)
C125	0.1714 (6)	0.4921 (7)	0.0807 (6)	5.1 (3)

C126	0.1081 (6)	0.4484 (6)	0.0721 (5)	3.6 (2)
C131	−0.0079 (5)	0.3196 (5)	0.0255 (4)	2.6 (2)
C132	−0.0772 (6)	0.3280 (6)	−0.0058 (5)	3.7 (2)
C133	−0.0883 (7)	0.3167 (7)	−0.0662 (5)	4.6 (3)
C134	−0.0307 (7)	0.2969 (7)	−0.0965 (4)	4.7 (3)
C135	0.0381 (6)	0.2866 (7)	−0.0671 (4)	4.1 (2)
C136	0.0503 (6)	0.2995 (6)	−0.0068 (5)	3.5 (2)
C211	0.1028 (5)	0.1429 (5)	0.0723 (4)	2.8 (2)
C212	0.1596 (6)	0.1902 (6)	0.0962 (5)	3.6 (2)
C213	0.2254 (6)	0.1905 (7)	0.0720 (6)	4.7 (3)
C214	0.2325 (6)	0.1432 (8)	0.0239 (6)	5.4 (3)
C215	0.1790 (6)	0.0950 (8)	0.0012 (5)	5.0 (3)
C216	0.1140 (6)	0.0931 (7)	0.0261 (4)	4.0 (2)
C221	0.0252 (6)	0.0419 (5)	0.1405 (4)	3.1 (2)
C222	0.0898 (7)	0.0212 (7)	0.1748 (5)	4.6 (3)
C223	0.0974 (8)	−0.0555 (8)	0.1983 (6)	6.1 (3)
C224	0.0418 (9)	−0.1086 (7)	0.1867 (6)	7.3 (4)
C225	−0.0222 (9)	−0.0869 (7)	0.1548 (6)	6.4 (4)
C226	−0.0301 (7)	−0.0117 (6)	0.1306 (5)	4.6 (3)
C231	−0.0621 (5)	0.1393 (5)	0.0546 (4)	2.5 (2)
C232	−0.0666 (6)	0.1279 (6)	−0.0065 (4)	3.6 (2)
C233	−0.1328 (8)	0.1284 (8)	−0.0401 (5)	5.4 (3)
C234	−0.1954 (7)	0.1427 (9)	−0.0167 (6)	5.9 (3)
C235	−0.1918 (6)	0.1530 (8)	0.0444 (5)	4.9 (3)
C236	−0.1259 (6)	0.1527 (7)	0.0801 (5)	4.2 (2)
B	0.238	0.210	0.276	16.0

Table 2. *Geometric parameters* (Å, °)

Pd—Cl1	2.386 (3)	Pd—P1	2.290 (2)
Pd—Cl2	2.354 (3)	Pd—P2	2.256 (2)
Cl1—Pd—Cl2	84.89 (9)	Cl2—Pd—P1	172.05 (9)
Cl1—Pd—P1	89.40 (9)	Cl2—Pd—P2	90.8 (1)
Cl1—Pd—P2	175.7 (1)	P1—Pd—P2	94.86 (9)

The tetrafluoroborate anion was refined as a rigid group (ideal tetrahedron with B—F distance of 1.415 Å) with isotropic thermal parameters, those of the F atoms being 20% larger than that of the B atom. Only three of the four F atoms of the BF_4 groups were obvious on the difference Fourier map, and their large temperature factors indicated some possible rotational disorder of this highly symmetric group, which could not be resolved. Hence the fourth F atom was introduced in an estimated position followed by group regularization (B—F = 1.415 Å). The tetrafluoroborate anion was refined further as a rigid group (ideal tetrahedron) with isotropic thermal parameters by means of the *CRYSTALS* program (available with the *MolEN* system), with thermal parameters of the F atoms being 20% larger than those of the B atom.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55805 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1035]

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Structure of Pentaaqua(L-serine)holmium(III) Trichloride

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Abstract

The crystal structure of a holmium(III) complex with L-serine $\{[Ho(C_3H_7NO_3)(H_2O)_5]Cl_3\}$ is reported. As for most cases of lanthanide complexes with amino acids, the coordination number is eight. Each Ho ion is coordinated by two carboxylate O atoms, one hydroxyl O atom of a serine molecule and five other O atoms from water molecules. The Cl anions are not coordinated.

Comment

The structure of the title compound was investigated in order to continue the study on interaction and coordination of lanthanide ions with amino acids (Głowiak, Dao, Legendziewicz & Huskowska, 1991, and references therein). The structure is that of a linear polymer, in which the Ho ions are connected by serine carboxylate groups. There is pseudosymmetry between the independent structure units of Ho(1) and Ho(2). On moving the cell origin to the point (−0.25, −0.148, 0), the approximate symmetry of the $P2_1/a$ space group could be demonstrated. Eight-coordinated polyhedra of Ho ions take the form of distorted square antiprisms [Δ_{SAP} values

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