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Dichloro(2,2':6',2''-terpyridyl-*N,N',N''*)-mercury(II)

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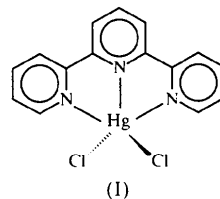
Abstract

In the title compound, [HgCl₂(C₁₅H₁₁N₃)], the Hg atom is coordinated by three N atoms from terpyridine at distances of 2.372 (4), 2.396 (5) and 2.430 (5) Å, and by two Cl atoms at distances of 2.419 (2) and 2.486 (2) Å, forming an irregular five-coordinate polyhedron.

Comment

In most mercury(II) structures, the Hg—L bonds are essentially covalent but, since they have different bond order, various coordination polyhedra are possible. They are conveniently categorized according to their characteristic (*m*; *m* = number of covalently bonded atoms) and effective coordination (*m* + *n*; *n* = number of atoms at distances shorter than the sum of the van der Waals radii) (Grdenić, 1965, 1981). Only four structures of mercury(II) complexes with terpyridine have been published so far, [(CH₃)Hg(Et₃terpy)]NO₃ (Canty *et al.*, 1981), Hg(CF₃)₂(terpy) (Kamenar *et al.*, 1982), Hg(OCOCF₃)₂(terpy) (Grdenić *et al.*, 1991) and the 2:1 solvate of [Hg(terpy)₂](CF₃SO₃)₂ with acetone (Matković-Čalogović *et al.*, 1995). The analogous complexes with mercury(II) halides, perchlorate and nitrate were identified only on the basis of chemical analysis and IR spectroscopy (Douglas & Wilkins, 1969), in which five-coordinate mercury was suggested for the halide and nitrate complexes HgX₂(terpy) (*X* = Cl[−], Br[−], I[−], NO₃[−]), and six-coordinate mercury for the perchlorate [Hg(terpy)₂](ClO₄)₂. Terpyridine is usually a tridentate ligand, as in the above-mentioned structures, but can also be bidentate, as in Ru(CO)₂X₂(terpy) (*X* = Cl[−], Br[−]) (Deacon *et al.*, 1984).

The present structural analysis, (I), shows that HgCl₂(terpy) also acts as a tridentate ligand with the shortest Hg—N bond of 2.372 (4) Å being the central one and two terminal bonds of 2.396 (5) and 2.430 (5) Å. Two Cl atoms additionally coordinate mercury at distances



of 2.419 (2) and 2.486 (2) Å forming an irregular five-coordinate polyhedron. The bond angles at Hg range from 68.1 (2) to 141.4 (1)°. The smallest angles are a consequence of the formation of the five-membered chelate rings and the largest (N21—Hg—Cl1) is associated with the shortest Hg—N and Hg—Cl bonds. That is not unusual since mercury has a tendency to form linear coordination which is often deformed by contacts with neighbouring ligands forming various irregular polyhedra.

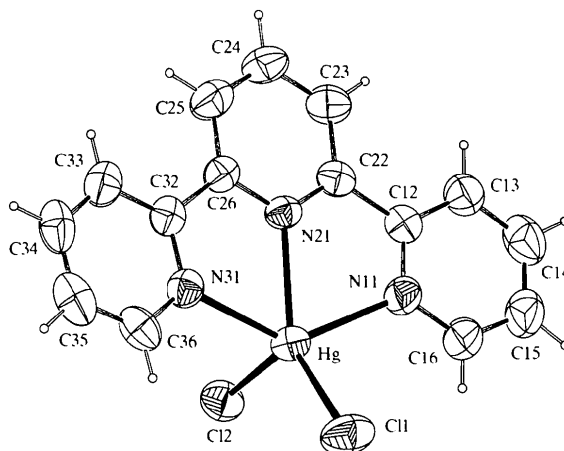


Fig. 1. An ORTEP view [obtained with PLATON (Spek, 1990)] of the molecule with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

In mercury complexes, there is a large span of Hg—N(terpyridine) distances depending upon the nature of the other ligand. In the organomercury compound [(CH₃)Hg(Et₃terpy)]NO₃, the Hg—N(central) bond of 2.26 (2) Å is much shorter than the two Hg—N(terminal) bonds [2.51 (2) and 2.61 (2) Å] and the C—Hg—N angle of 171 (1)° is close to linear forming an effective [2+2] coordination sphere. When two strong Hg—C bonds are formed, as in Hg(CF₃)₂(terpy), terpyridine is bound weakly with three Hg···N interactions ranging from 2.62 (3) to 2.70 (2) Å completing a [2+3] coordination sphere. In the present structure, the Hg—N bonds are within the range of values found in the six-coordinate [Hg(terpy)₂]²⁺ cation [2.27 (2)–2.53 (2) Å] (Matković-Čalogović *et al.*, 1995). The Hg—N(terminal) bonds are longer in the present structure in comparison with Hg(OCOCF₃)₂(terpy) which is also five-coordinate [Hg—N 2.35 (1), 2.36 (1) and 2.37 (1) Å].

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Upon coordination, terpyridine adopts a *cis,cis* geometry in contrast to *trans,trans* in the uncoordinated state (Bessel *et al.*, 1992). It also undergoes distortions that enable the terminal pyridines to have a closer approach to the Hg atom. The largest distortions involve the decrease of the N—C—C angles within the five-membered chelate ring [115.9(5)–116.7(5)°] and the increase of N11—C16—C15 and N31—C36—C35 to 123.9(7) and 122.9(7)°, respectively.

There are only van der Waals contacts between the molecules.

The band group between 1600 and 1400 cm⁻¹ is of particular interest in terms of the mode of terpy coordination. Four $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$ skeletal vibrations of the free terpyridine are split into eight bands due to complexation. The shift of the 'ring breathing' vibrations observed at 1020 cm⁻¹ with respect to the free ligand (988 cm⁻¹) is consistent with coordinated terpyridine (Sinha, 1965). Very strong absorption due to the ring H atoms is observed at 767 cm⁻¹.

Experimental

Slow evaporation of ethanolic solutions of the starting reagents at room temperature yielded crystals suitable for X-ray structure determination. The IR spectrum in the region 4000–450 cm⁻¹ was recorded on a Perkin-Elmer FT-IR spectrophotometer Model 1600 using a KBr disc. IR maximum (cm⁻¹): 3055 (*w-m*), 1595 (*m-s*), 1588 (*s*), 1580 (*s*), 1564 (*m-s*), 1550 (*m*), 1474 (*s*), 1448 (*vs*), 1432 (*s*), 1310 (*m-s*), 1269 (*w-m*), 1250 (*m*), 1195 (*w*), 1165 (*w*), 1155 (*w*), 1020 (*s*), 767 (*vs*), 650 (*m*), 636 (*m*).

Crystal data

[HgCl₂(C₁₅H₁₁N₃)]
M_r = 504.76
 Monoclinic
*P*2₁/*c*
a = 11.095 (4) Å
b = 8.280 (6) Å
c = 16.445 (4) Å
 β = 94.02 (2)°
V = 1507.0 (13) Å³
Z = 4
D_x = 2.225 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 30 reflections
 θ = 15–23°
 μ = 10.562 mm⁻¹
T = 293 (2) K
 Prism
 0.315 × 0.210 × 0.165 mm
 Colourless

Data collection

Philips PW1100 diffractometer updated by Stoe
 ω -2 θ scans
 Absorption correction: by integration (Stoe & Cie, 1995b)
T_{min} = 0.152, *T_{max}* = 0.235
 6308 measured reflections
 4395 independent reflections
 2668 reflections with $F_o > 4\sigma(F_o)$
R_{int} = 0.040
 θ_{max} = 30.01°
h = -15 → 15
k = 0 → 11
l = 0 → 23
 4 standard reflections
 frequency: 90 min
 intensity decay: 22.8%

Refinement

Refinement on *F*²
R(*F*) = 0.041
 $wR(F^2)$ = 0.105
S = 0.992
 4362 reflections
 190 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.949 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.114 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Hg—N11	2.430 (5)	Hg—Cl1	2.419 (2)
Hg—N21	2.372 (4)	Hg—Cl2	2.486 (2)
Hg—N31	2.396 (5)		
N21—Hg—N31	68.7 (2)	Cl1—Hg—N11	98.57 (14)
N21—Hg—Cl1	141.42 (13)	N21—Hg—Cl2	104.57 (12)
N31—Hg—Cl1	108.57 (13)	N31—Hg—Cl2	97.45 (13)
N21—Hg—N11	68.1 (2)	Cl1—Hg—Cl2	113.81 (7)
N31—Hg—N11	135.5 (2)	N11—Hg—Cl2	103.04 (14)

Intensities were corrected for decay, Lorentz, polarization and absorption effects. The positions of Hg atoms were located by the Patterson method, while the subsequent full-matrix least-squares refinement based on *F*² and difference Fourier maps revealed all non-H atoms. The H-atom positions were calculated geometrically (riding model, *U_{eq}* = 1.2*U_{eq}* of parent atom). Final full-matrix least-squares refinement of the coordinates and anisotropic displacement parameters for non-H atoms reduced *R* to 0.041. The maximum density in the final difference Fourier map was 0.84 Å from Hg.

Data collection: *STADIA* (Stoe & Cie, 1995a). Cell refinement: *STADIA*. Data reduction: *X-RED* (Stoe & Cie, 1995b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965) and *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1361). Services for accessing these data are described at the back of the journal.

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Bis(dihydrogen phosphato-*O*)[(1*SR*,4*SR*,-8*RS*,11*RS*)-1,4,8,11-tetraazacyclotetradecane- κ^4 N]nickel(II)

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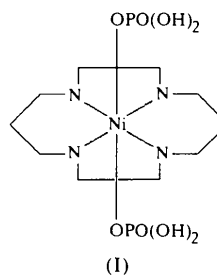
Abstract

The Ni^{II} ion in the title compound, [Ni(H₂PO₄)₂·(C₁₀H₂₄N₄)], is six-coordinate in a distorted square bipyramidal environment. The crystal structure consists of two molecules of the title compound, each residing on a centre of inversion. Four tetramine N atoms of the macrocyclic ligand are equatorial [average Ni—N distance = 2.07 (1) Å] and two O atoms, one from each dihydrogen phosphate ion, are axial [average Ni—O distance = 2.12 (3) Å]. The structure of the title complex consists of a three-dimensional framework, which delimits intersecting *a*-axis, *b*-axis and *c*-axis tunnels. Two types of hydrogen bonds, O—H···O and N—H···O, ensure the cohesion and stability of the molecular packing.

Comment

The Ni^{II} complexes of cyclic tetramines have been studied extensively because of their diverse stereochemistry. We describe here the crystal structure of the title compound, (I). There are two crystallographically distinct molecules in the asymmetric unit. The coordination geometry around each of the central atoms is the same, while the interatomic distances and angles

differ slightly between the two units centred on Ni1 and Ni2. These units are stacked in alternating sheets normal to the *c* axis at *z* = 0 and *z* = $\frac{1}{2}$, respectively. In each sheet, the molecules centred on Ni1 and Ni2 are connected by strong hydrogen bonds to form ribbons running along [010] and [100], respectively. The sheets are held together by hydrogen bonds established between ribbons in perpendicular directions, giving rise to a three-dimensional framework which delimits intersecting tunnels. Each [Ni(C₁₀H₂₄N₄)] group is anchored by N—H···O hydrogen bonds to different H₂PO₄⁻ tetrahedra. The latter anion is connected to three other anions through strong O—H···O hydrogen bonds to form infinite ribbons spreading in the [001] direction.



The coordination geometry around each Ni^{II} ion is slightly distorted square bipyramidal with four equatorial N atoms and two axial O atoms. The configurations of the four chiral N-atom centres are 1*SR*, 4*SR*, 8*RS* and 11*RS*. The Ni—N distances [2.056 (1)–2.090 (1) Å] agree with corresponding values found in similar nickel complexes (Mukherjee *et al.*, 1995). The observed lengthening of Ni1—O1 [2.099 (1) Å] and Ni2—O5 [2.141 (1) Å] compared with Ni—N may be due to steric constraints introduced by the coordinating bulky H₂PO₄ ligand. These distances are similar to those reported for [*N*-(3-aminopropyl)-1,3-propanedi-

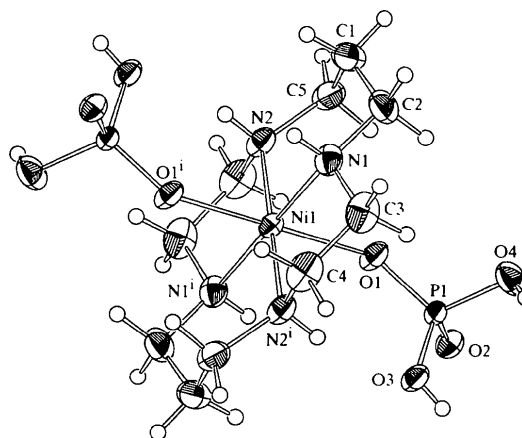


Fig. 1. ZORTEP (Zsolnai, 1994) probability view (50%) of one of the two independent molecules of (I). H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $-x, -y, -z$.]