

Cu—O2	2.645 (2)	0.073†		2.583 (2)	0.087†	
Cu—N1	1.974 (1)	0.494†		1.977 (2)	0.490	
O1—C10	1.268 (2)	1.549	2.00 (5)	1.274 (3)	1.524	1.97 (5)
O1—Cu	1.973 (1)	0.452		1.974 (2)	0.451	
O2—C10	1.241 (2)	1.667	1.86 (5)	1.237 (3)	1.685	1.90 (5)
O2—Cu	2.645 (2)	0.073		2.583 (2)	0.087	
O2···H10	2.04 (3)	0.122		2.02 (4)	0.128	

† Occurs twice around the *i* atom.

The title structures were solved by the conventional Patterson method and were refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically.

For both compounds, data collection: *KM-4 Software* (Kuma Diffraction, 1992); cell refinement: *KM-4 Software*; data reduction: *DATARED* in *KM-4 Software*; program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 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: JZ1349). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1234–1236

Hydroxotriphenyltin 2,6-bis(1*H*-benzimidazol-2-yl)pyridine hydrate

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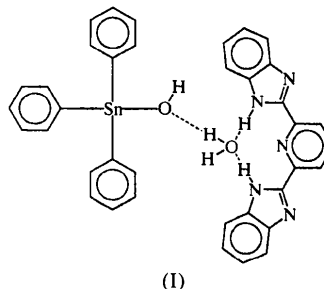
(Received 11 February 1999; accepted 15 March 1999)

Abstract

In hydroxotriphenyltin 2,6-bis(1*H*-benzimidazol-2-yl)pyridine hydrate (1/1/1), [Sn(C₆H₅)₃(OH)]·C₁₉H₁₃N₅·H₂O, the water molecule is hydrogen bonded to the hydroxo O atom, the two imino N atoms of the benzimidazolyls flanking the pyridine unit and one of the two amino N atoms of an adjacent *N*-heterocycle [O···O = 2.680 (5) Å; O···N = 2.831 (5), 2.930 (6) and 2.767 (6) Å]. The hydrogen-bonding architecture gives rise to a two-dimensional network structure in which alternate *N*-heterocycles are stacked perpendicular to each other when the structure is viewed along the *z* axis. The organotin moiety shows tetrahedral coordination at tin.

Comment

Hydroxotriphenyltin, a reagent used in the synthesis of a plethora of triphenyltin complexes, exists as hydroxo-bridged linear chains whose Sn atoms show *trans*-trigonal-bipyramidal coordination [Sn—O = 2.197 (5) and Sn←O = 2.255 (5) Å; Glidewell & Liles, 1978]. This compound is not known to afford adducts (Harrison, 1995), so that the title compound, (I), represents an unusual example of a hydroxotriphenyltin complex.



A view of the asymmetric unit of (I) is shown in Fig. 1. The two N—H groups of the 2,6-bis(benzimidazol-2-yl)pyridine molecule form N—H···O hydrogen bonds to the water molecule (details in Table 2); the water molecule is, in turn, hydrogen

bonded (O—H···O) to the hydroxotriphenyltin moiety and also to the N atom (O—H···N) of an adjacent 2,6-bis(benzimidazol-2-yl)pyridine molecule. The OH group of the triphenyltin moiety forms an O—H···N bond with the remaining N atom of another 2,6-bis(benzimidazol-2-yl)pyridine molecule. The central pyridyl N atom is not involved in any hydrogen bonding.

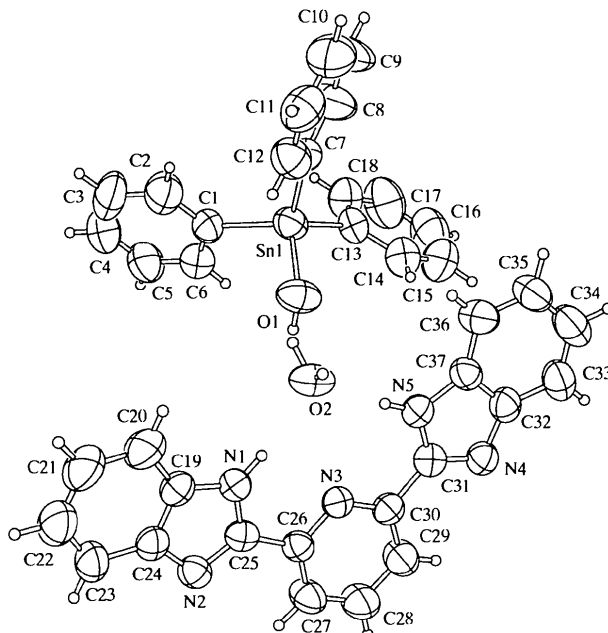


Fig. 1. ORTEPII (Johnson, 1976) plot of (I) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

The hydroxotriphenyltin moiety has an Sn—O bond length which is uncharacteristically short [Sn—O = 1.961 (3) Å]; covalent Sn—O bonds shorter than 2.0 Å have been found in bis(triorganotin) oxides, but these are generally associated with a nearly linear Sn—O—Sn skeleton arising from *sp* hybridization at oxygen (Lockhart *et al.*, 1989). In the 2,6-bis(benzimidazol-2-yl)pyridine molecule, the two benzimidazolyl moieties are only marginally twisted relative to the central pyridyl ring [dihedral angles = 2.5 (3) and 5.7 (3)°]. The entire *N*-heterocycle can almost be regarded as a planar entity (r.m.s. deviation = 0.060 Å); the water molecule lies within this plane, being displaced out of it by only 0.053 (4) Å.

Experimental

2,6-Bis(benzimidazol-2-yl)pyridine was synthesized from the reaction between pyridine-2,6-dicarboxylic acid and *o*-phenylenediamine (Addison & Burke, 1981). The title compound was obtained in an unsuccessful attempt at linking the *N*-heterocycle to a triphenylstannyl entity through an Sn—N bond. Equimolar quantities of the *N*-heterocycle and triphenyltin hydroxide were heated in ethanol until the reactants dissolved completely; the compound separated on cooling the solution.

Crystal data

[Sn(C₆H₅)₃(OH)]·C₁₉H₁₃N₅·
H₂O
M_r = 696.36
Monoclinic
*P*2₁/*a*
a = 12.248 (2) Å
b = 14.377 (1) Å
c = 19.150 (2) Å
β = 103.547 (11)°
V = 3278.3 (7) Å³
Z = 4
D_x = 1.411 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
ω-2*θ* scans
Absorption correction:
ψ scan (North *et al.*,
1968)
T_{min} = 0.794, *T_{max}* = 0.835
6102 measured reflections
5801 independent reflections

Refinement

Refinement on *F*²
R[*F*² > 2*σ*(*F*²)] = 0.052
wR(*F*²) = 0.127
S = 0.959
5801 reflections
406 parameters
H atoms riding, *U*(H) =
1.5*U_{eq}*(C,N,O)

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 12.0–14.0°
μ = 0.820 mm⁻¹
T = 298 (2) K
Block
0.29 × 0.29 × 0.22 mm
Colorless

3650 reflections with
I > 2*σ*(*I*)
R_{int} = 0.044
θ_{max} = 25.05°
h = 0 → 14
k = 0 → 17
l = -22 → 22
3 standard reflections
frequency: 60 min
intensity decay: none

w = 1/[*σ*²(*F_o*²) + (0.0674*P*)²]
where *P* = (*F_o*² + 2*F_c*²)/3
(*Δ*/*σ*)_{max} < 0.001
Δρ_{max} = 0.862 e Å⁻³
Δρ_{min} = -0.323 e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Sn1—O1	1.961 (3)	Sn1—C13	2.114 (6)
Sn1—C7	2.103 (5)	Sn1—C1	2.124 (6)
O1—Sn1—C7	102.8 (2)	C1—Sn1—C7	115.5 (2)
O1—Sn1—C13	107.2 (2)	C1—Sn1—C13	111.2 (2)
O1—Sn1—C1	106.8 (2)	C7—Sn1—C13	112.4 (2)

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···N2'	0.96	1.89	2.821 (5)	162
O2—H2A···N4 ⁱⁱ	0.97	1.81	2.767 (6)	168
O2—H2B···O1	0.97	1.89	2.680 (5)	136
N1—H1N···O2	0.86	1.98	2.832 (5)	170
N5—H5N···O2	0.86	2.08	2.930 (6)	171

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

Data collection: CAD-4 VAX/PC (Enraf–Nonius, 1988). Cell refinement: CAD-4 VAX/PC. Data reduction: NRCVAX (Gabe *et al.*, 1989). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: ORTEPII (Johnson, 1976). 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: FG1540). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1236–1238

Di- μ -chloro-bis{[tris(2-pyridylmethyl)amine- κ^4 N]nickel(II)} bis(triethylammonium) tetraperchlorate

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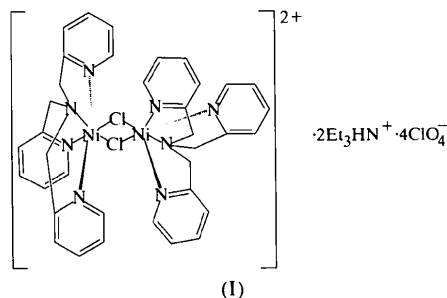
(Received 2 February 1999; accepted 28 April 1999)

Abstract

The title compound, (C₆H₁₆N)₂[Ni₂Cl₂(C₁₈H₁₈N₄)₂](ClO₄)₄ or [{Ni(TPA)Cl}]₂(ClO₄)₂·2HN(CH₂CH₃)₃·ClO₄, where TPA is tris(2-pyridylmethyl)amine, consists of a centrosymmetric dimeric nickel(II) center bridged asymmetrically by Cl[−] ions. The difference in the Ni—Cl distances [0.141 Å for 2.3655 (8) and 2.507 (1) Å] is the largest thus far reported. Each Ni atom is pseudo-octahedral six-coordinate. Triethylammonium perchlorate cocrystallizes with the metal complex.

Comment

We have considerable interest in metal complexes of TPA [tris(2-pyridylmethyl)amine] and upon reading the introduction of a recent article (Bebout *et al.*, 1997), we noted that Ni^{II} complexes of TPA were not mentioned in a list of known TPA–metal complexes. After we had synthesized the title complex, (I), we found that the crystal structures of three Ni^{II}–TPA complexes had been reported previously (Ito & Takita, 1996; Zhang *et al.*, 1996).



The cationic portion of the title complex is a centrosymmetric unit of two Ni atoms bridged unsymmetrically by two Cl atoms. The separation of the two Ni atoms is 3.525 (1) Å, and the Cl separation is 3.367 (2) Å. The Ni atoms are pseudo-octahedral six-coordinate, with four N atoms from the TPA ligand completing the coordination environment. The difference in the Ni—Cl distances (0.141 Å) is the largest of any Ni₂Cl₂ core reported (see, for example, Bkouche-Waksman *et al.*, 1981; Ianneli *et al.*, 1991; Blake *et al.*, 1996; Di Vaira *et al.*, 1997). As expected, in the reported structures, the greatest differences are observed for cases in which the types of donor atoms *trans* to the bridges are the most different. In the present case, the difference in Lewis basicity of the tertiary amine compared to that of pyridine is quite pronounced, as reflected in the Ni—Cl distances. The shortest Ni—Cl distance [2.3655 (8) Å] is *trans* to the tertiary amine of TPA. In many structures, the Lewis basicity difference between the tertiary amine and pyridine of TPA further manifests itself as a longer metal-to-nitrogen distance for the tertiary amine (see, for example, Norman *et al.*, 1990; Dalley *et al.*, 1996). That is not the case here where the Ni—N distances are all similar. The distances and angles within the dimeric Ni^{II} unit are the same within experimental error as those reported previously for [{Ni(TPA)Cl}]₂(ClO₄)₂·H₂O (Zhang *et al.*, 1996).

We found five examples of triethylammonium perchlorate cocrystallizing with a metal complex (Kato & Ito, 1986; Gomez-Romero *et al.*, 1988; Das & Nag, 1991; Gluziński *et al.*, 1993; Thuéry *et al.*, 1995). The metrical parameters in the title complex are unremarkable. The triethylammonium ion hydrogen bonds to a perchlorate; the separation of O6 to N5 of a triethyl-