Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.086$
$S = 1.035$
2163 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.2858P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.455$ e Å^{-3}
$\Delta\rho_{min} = -0.503$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0041 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—O1	1.952 (2)	C1—C11	1.505 (4)
Cu—O2	2.764 (3)	C2—C3	1.404 (4)
Cu—N1	2.046 (2)	C3—C4	1.357 (5)
O1—C1	1.272 (3)	C5—C4	1.377 (5)
N1—C2	1.350 (3)	C6—C5	1.377 (4)
N1—C6	1.361 (3)	C6—C7	1.487 (4)
O2—C1	1.235 (3)	N2—C2	1.356 (3)
O1—Cu—N1	91.59 (9)	O1—C1—C11	116.1 (3)
O1—Cu—O2	52.38 (7)	N1—C2—N2	117.7 (2)
N1—Cu—O2	86.98 (9)	N1—C2—C3	121.3 (2)
C1—O1—Cu	111.04 (16)	N2—C2—C3	121.1 (2)
C2—N1—C6	119.1 (2)	N1—C6—C5	120.9 (3)
C2—N1—Cu	119.04 (16)	N1—C6—C7	117.4 (2)
C6—N1—Cu	121.10 (18)	C5—C6—C7	121.7 (3)
C1—O2—Cu	73.39 (16)	C4—C3—C2	118.8 (3)
O2—C1—O1	123.2 (2)	C4—C5—C6	119.7 (3)
O2—C1—C11	120.7 (3)	C3—C4—C5	120.1 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1···O2	0.86	2.36	2.952 (3)	126
N2—H2···O2^{i}	0.86	2.14	2.922 (4)	151

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

H atoms were included at calculated positions using *SHELXL*97 (Sheldrick, 1997) and refined using a riding model, with isotropic displacement parameters taken from the parent atoms and multiplied by 1.5 for methylenic and methyl H atoms, and by 1.2 for amino and phenyl H atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994). Cell refinement: *XRAY*76 (Stewart *et al.*, 1976). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1255). Services for accessing these data are described at the back of the journal.

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Di-μ-chloro-bis(aquachlorodimethyltin)–dichlorodimethyl[2,4,6-tris(2-pyridyl)-1,3,5-triazine]tin (1/2)

Kong Mun Lo,[a] V. G. Kumar Das[a] and Seik Weng Ng[b]

[a]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and* [b]*Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: h1nswen@umcsd.um.edu.my*

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Abstract

In the centrosymmetric title compound, $[Sn_2(CH_3)_4Cl_4(H_2O)_2]\cdot 2[Sn(CH_3)_2Cl_2(C_{18}H_{12}N_6)]$, the Sn atom of the dichlorodimethyl[2,4,6-tris(2-pyridyl)-1,3,5-triazine]tin moiety is seven-coordinate in a *trans*-$C_2SnCl_2N_3$ pentagonal bipyramidal geometry [C—Sn—C 157.0(2)°] and that of the water-coordinated di-μ-chloro-bis(aquachlorodimethyltin) moiety is six-coordinate in a *trans*-C_2SnCl_3O octahedral geometry [C—Sn—C 146.2 (2)°]. In the water-coordinated moiety, the Sn···Cl bridge [3.425 (2) Å] is *trans* to the Sn—O$_{water}$ bond [2.391 (4) Å]; each water molecule is linked to a free pyridyl N atom of the heterocycle by only one hydrogen bond [O···N 2.821 (6) Å].

Comment

2,2′:6′,2″-Terpyridyl when treated with dimethyltin diisothiocyanate affords a seven-coordinate *N*,*N*′,*N*″-

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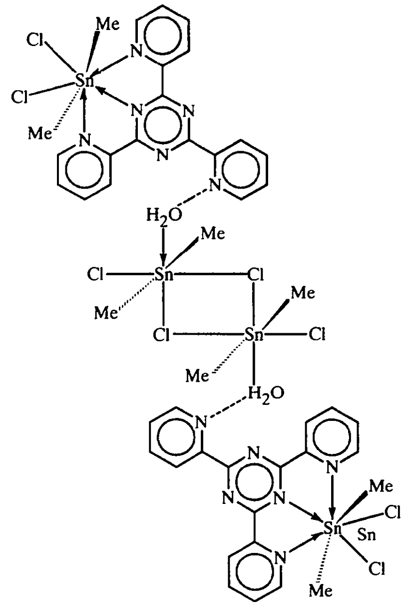
chelated adduct having a nearly linear [C—Sn—C 173.7 (2)°] C_2Sn skeleton [Sn—N distances of 2.479 (3), 2.497 (3) and 2.570 (4) Å; Naik & Scheidt, 1973]. In the reaction with dimethyltin dichloride, a stronger Lewis acid, the heterocycle displaces a Cl^- ion to furnish dimethylchloro(terpyridyl)tin dimethyltrichlorostannate, a salt with Sn in both five- and six-coordinate geometries, the heterocycle binding much more strongly through its nitrogen ends [Sn—N 2.29 (3), 2.33 (4) and 2.41 (3) Å; Einstein & Penfold, 1968]. Tris(2-pyridyl)-1,3,5-triazine (Drew *et al.*, 1998) demonstrates a similar tridentate binding ability towards dimethyltin dichloride in the title compound, (I), which consists of two dichlorodimethyl[2,4,6-tris(2-pyridyl)-1,3,5-triazine]tin moieties that are hydrogen bonded to a centrosymmetric di-μ-chloro-bis(aquachlorodimethyltin) moiety. Unlike monodentate *N*-donor ligands such as the imidazoles that readily form complexes with dimethyltin dichloride (Casellato *et al.*, 1992), bidentate or tridentate *N*-donor ligands tend to yield hydrates instead of 1:1 adducts, particularly when the reactions are carried out in moist solvents (Cunningham *et al.*, 1988; Valle *et al.*, 1988). The seven-coordinate dichlorodimethyl[2,4,6-tris(2-pyridyl)-1,3,5-triazine]tin moiety of the title compound represents an unusual example of a dimethyltin dichloride complex with a tridentate nitrogen heterocycle; such a compound has not been noted previously in the literature on organotin compounds (Harrison, 1995). The *trans*-$C_2SnCl_2N_3$ pentagonal bipyramidal coordination [C—Sn—C 157.0 (2)°] is distorted, as shown by the length of the Sn—N bonds [2.694 (4), 2.847 (4) and 2.931 (5) Å]. The bonds are much longer than those found in the dimethyltin diisothiocyanate–terpyridyl adduct, as well as the corresponding distances [Sn—N 2.268 (5), 2.295 (6) and 2.326 (6) Å] found in the [6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridyl]dimethyltin cation (Constable *et al.*, 1985).



(I)

The coordination number of the Sn atom in the di-μ-chloro-bis(aquachlorodimethyltin) moiety increases to six owing to an Sn···Cl bridge. Sixfold coordination in 1:1 adducts of dimethyltin dichloride with monodentate

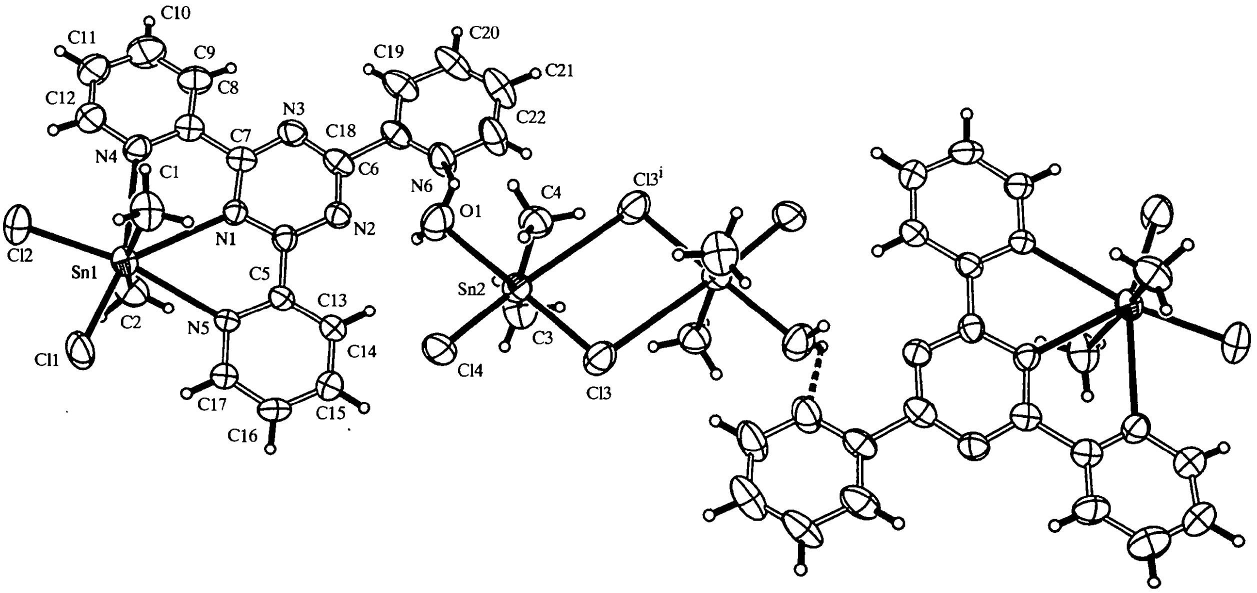


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $-x$, $-1-y$, $1-z$.]

O-donor ligands is readily achieved through such tin–chlorine bridging, this feature being documented in a number of such adducts (Ng & Rheingold, 1989). The C—Sn—C angle is related to the strength of the bridge; the closer the bridging Cl atom, the wider the C—Sn—C angle, which has been opened up from the idealized value of 120° expected for sp^2-hybridized Sn. The C—Sn—C angle [146.2 (2)°] in the moiety exceeds that [137.7 (2)°] found in the dimethyltin dichloride adduct with 3-methyl-4-nitropyridine *N*-oxide, but the Sn···Cl bridge [3.425 (2) Å] is distinctly shorter than that of the 3-methyl-4-nitropyridine *N*-oxide adduct [3.934 (1) Å; Lim & Ng, 1998]. The dinuclear di-μ-chloro-bis(aquachlorodimethyltin) entity also exists in di-μ-chloro-bis(aquachlorodimethyltin)·18-crown-6 (Amini *et al.*, 1984).

The packing of organotin hydrates is characterized by the compounds maximizing the number of hydrogen-bonding interactions; for example, in the aquadimethyltin dichloride crown-ether complexes, the water molecule forms four hydrogen bonds (Amini *et al.*, 1984, 1994). The title structure features one short and one long $N_{pyridyl}\cdots O_{water}$ hydrogen bond [2.821 (6) and 3.197 (6) Å, respectively], which appears to be an anomaly. As the 1-triazinyl N atom of the 1,3,5-triazine fragment and the N atoms belonging to the 2-pyridyl and 6-pyridyl substituents are already being used {to chelate to Sn to form the dichlorodimethyl[2,4,6-tris(2-pyridyl)-1,3,5-triazine]tin moiety}, only the N atom of the 4-pyridyl ring and the 3-triazinyl N atom would be capable of interacting with the coordinated water molecule. However, the nitrogen heterocycle is planar (Drew *et al.*, 1998), a feature that has been noted in other tris(2-pyridyl)-1,3,5-triazine complexes (Schödel, 1995; Ng, 1998), so that a shorter hydrogen bond, if formed, would place the $O_{water}\cdots N_{3-azinyl}$ interaction too close to the 2-pyridyl ring in the crystal structure.

Experimental

Equimolar quantities of dichlorodimethyltin and tris(2-pyridyl)-1,3,5-triazine were dissolved in hot ethanol. The title compound separated on cooling the solution.

Crystal data

$[Sn_2(CH_3)_4Cl_4(H_2O)_2]\cdot$-
$2[Sn(CH_3)_2Cl_2(C_{18}H_{12}N_6)]$
$M_r = 1539.34$
Monoclinic
$P2_1/n$
$a = 10.395 (2)$ Å
$b = 13.320 (3)$ Å
$c = 21.162 (2)$ Å
$\beta = 100.414 (9)°$
$V = 2881.9 (9)$ Å^3
$Z = 2$
$D_x = 1.774$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.0–14.0°$
$\mu = 2.131$ mm^{-1}
$T = 298 (2)$ K
Block
0.29 × 0.22 × 0.22 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.612$, $T_{max} = 0.651$
5351 measured reflections
5052 independent reflections

3628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = -25 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.088$
$S = 0.977$
5052 reflections
316 parameters
H atoms riding, $U(H) = 1.5U_{eq}(C,O)$

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.502$ e Å^{-3}
$\Delta\rho_{min} = -0.474$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sn1—C1	2.083 (6)	Sn2—C3	2.103 (6)
Sn1—C2	2.099 (6)	Sn2—C4	2.099 (6)
Sn1—Cl1	2.461 (2)	Sn2—O1	2.391 (4)
Sn1—Cl2	2.520 (2)	Sn2—Cl3	2.493 (2)
Sn1—N1	2.847 (4)	Sn2—Cl4	2.367 (2)
Sn1—N4	2.931 (5)	Sn2···Cl3^i	3.425 (2)
Sn1—N5	2.694 (4)		
C1—Sn1—C2	157.0 (2)	C2—Sn1—Cl2	97.5 (2)
C1—Sn1—N1	76.6 (2)	N1—Sn1—N4	56.3 (1)
C1—Sn1—N4	82.3 (2)	N1—Sn1—N5	59.0 (1)
C1—Sn1—N5	86.2 (2)	N1—Sn1—Cl1	141.2 (1)
C1—Sn1—Cl1	100.6 (2)	N1—Sn1—Cl2	134.1 (1)
C1—Sn1—Cl2	95.4 (2)	N4—Sn1—N5	115.3 (1)
C2—Sn1—N1	80.7 (2)	N4—Sn1—Cl1	162.5 (1)
C2—Sn1—N4	81.9 (2)	N4—Sn1—Cl2	78.0 (1)
C2—Sn1—N5	85.6 (2)	C3—Sn2—C4	146.2 (2)
C2—Sn1—Cl1	99.5 (2)		

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

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: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

We thank the National Science Council for R&D (IRPA 09-02-03-0004 and 09-02-03-0371) for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1251). Services for accessing these data are described at the back of the journal.

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A nickel complex with a tetradentate N_2S_2 Schiff base ligand

Ligia Gomes, Eulalia Pereira and Baltazar de Castro

CEQUP/Departamento de Química, Faculdade de Ciências do Porto, R. Campo Alegre 687, 4150 Porto, Portugal.
E-mail: bcastro@fc.up.pt

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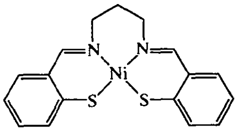
Abstract

The title compound, {2,2′-[1,3-propanediylbis(nitrilomethylidyne)]dibenzenethiolato(2−)-*S*,*N*,*N*′,*S*′}nickel(II) 1,4-dioxane 0.25-solvate, $[\mathrm{Ni(C_{17}H_{16}N_2S_2)}]\cdot 0.25\mathrm{C_4H_8O}$, has the $\mathrm{Ni^{II}}$ atom coordinated by a tetradentate ligand through two N and two S atoms. The complex has a *cis* configuration, imposed by the chelate ligand, in a tetrahedrally distorted planar environment.

Comment

Ligands containing thiolate donors have attracted much attention in recent years due to their potential use as models for the active centre of metalloproteins, especially for nickel-dependent oxidoreductases, where a sulfur-rich environment for the metal has been proposed (Hausinger, 1997; Kolodziej, 1994). Nickel(II) complexes with tetradentate Schiff bases have been frequently used to probe the structural and electronic consequences of small modifications of the ligand skeleton, namely changes in the polymethylene bridge between the nitrogen donors and the introduction of substituents into the salicylate fragment. On the other hand, and in contrast to what is found for N_2O_2 Schiff bases, there have been no systematic studies on the structural modifications induced by small changes in the ligand skeleton for NiN_2S_2 complexes or by O/S replacement in this type of complex.

In the course of a systematic study on S/O replacement in nickel(II) complexes (de Castro *et al.*, 1997; Pereira *et al.*, 1998), we have prepared and studied the title compound, [Ni(t-salpd)]. Details of the physicochemical characterization will be published elsewhere (Gomes *et al.*, 1999). The X-ray structure (Fig. 1) shows that the asymmetric unit contains two independent nickel complex molecules and half a molecule of solvent (1,4-dioxane), which lies across a centre of inversion. Both complex molecules have a *cis*-N_2S_2 coordination sphere around the $\mathrm{Ni^{II}}$ atom, showing an approximately square-planar geometry, with a small tetrahedral distortion. The dihedral angles between the N—Ni—S coordination planes are 10.60 (3) and 7.64 (3)° for molecules *A* and *B*, respectively, and the maximum deviation of the Ni, N and S atoms from the N_2S_2 best plane is less than 0.144 (1) Å for molecule *A* and less than 0.101 (1) Å for molecule *B*. Metal–ligand bonds are within the expected range for Schiff base nickel(II) complexes. The analogous complex with a dimethylene bridge between nitrogen donors, [Ni(t-salen)], shows a very similar structure but with a smaller tetrahedral distortion (Yamamura *et al.*, 1993). The different tetrahedral distortion is reflected in the Ni—N bond lengths, which are clearly longer in the present compound, probably because of the higher stereochemical demand of the propylene bridge. The increase in Ni—N bond lengths due to the replacement of the dimethylene bridge by a trimethylene bridge is also observed in nickel(II) complexes with related N_2O_2 Schiff bases (Carrondo *et al.*, 1993; Drew *et al.*, 1985).



[Ni(t-salpd)]

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