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Bis[2,2'-iminodipyridinium(1+)] Bis[μ-4-hydroxy-2,6-pyridinedicarboxylato(3–)]bis[aquadibutyltin(IV)] Dihydrate†

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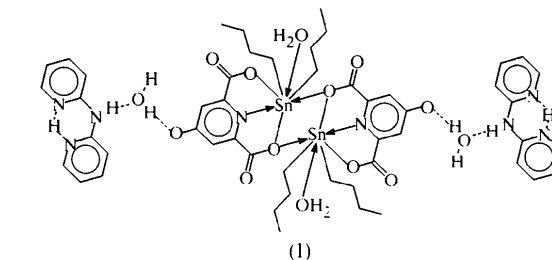
Abstract

The water-coordinated Sn atom in the centrosymmetric title compound, $(C_{10}H_{10}N_3)_2[Sn_2(C_7H_2NO_5)_2(C_4H_9)_4(H_2O)_2].2H_2O$, is seven-coordinate in a *trans*-C_2SnNO_4 pentagonal-bipyramidal geometry [C—Sn—C 156.6 (1)°]. The dianion is linked to two planar 2,2'-iminodipyridinium(1+) cations through the lattice water molecules *via* the amino bridges [O_{water}···N_{amino} 2.810 (5), O_{water}···$O_{hydroxy}$ 2.633 (4) and O_{water}···$O_{carbonyl}$ 2.927 (5) Å]. A weaker water–water interaction connects the ion pair into a linear helical chain.

Comment

Dibutyltin oxide condenses with dicyclohexylammonium 2,6-pyridinedicarboxylate to yield bis(dicyclohexylammonium) bis[dibutyl(2,6-pyridinedicarboxylato)stannate] (Ng *et al.*, 1997), but with methylphenylammonium 2,6-pyridinedicarboxylate to give bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] *N*-methylaniline solvate (Ng, 1998*b*). In the *N*-methylaniline solvate,

the dinuclear organotin moiety is linked by hydrogen bonds into layers, and disordered *N*-methylaniline molecules occupy the space between the wavy sheets. There are no hydrogen bonds connecting the sheets and the solvent molecules. This architecture is also found in bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] di-2-pyridylamine (1:1) (Ng, 1996). The sheets and the di-2-pyridylamine molecules are expected to be linked by hydrogen bonds in the hydroxy-substituted analog, bis[aquadibutyl(4-hydroxy-2,6-pyridinedicarboxylato)tin] di-2-pyridylamine, but its attempted synthesis gave instead isomeric bis[2,2'-iminodipyridinium(1+)] bis[aquadibutyl(4-hydroxy-2,6-pyridinedicarboxylato)tin] as a dihydrate. In this compound, the negative charges of the dianion reside formally on the 4-hydroxy O atoms. The negative charges also reside on the 4-hydroxy O atoms in bis-(diisopropylammonium) bis[aquadibutyl(4-hydroxy-2,6-pyridinedicarboxylato)tin] (Ng, 1998*a*), and the two compounds exemplify two ionic organotin compounds whose negative charges do not reside on the Lewis-acidic Sn atom.

The water-coordinated Sn atom in the title centrosymmetric dihydrate, (I), is seven-coordinate in a *trans*-C_2SnNO_4 pentagonal-bipyramidal geometry [C—Sn—C 156.6 (1)°], and the 4-hydroxy-2,6-pyridinedicarboxylato group bonds to the Sn atom through its O, N and O atoms. Both carboxyl groups are monodentate; however, one is bonded to just one Sn atom [Sn—O 2.125 (2) Å], whereas the other is bonded to two Sn atoms [Sn—O 2.299 (2) and 2.939 (2) Å]. Bond dimensions involving the Sn atom are similar to those found in bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] (Huber *et al.*, 1989) and bis(diisopropylammonium) bis[aquadibutyl(4-hydroxy-2,6-pyridinedicarboxylato)tin] (Ng, 1998*a*). Of the two Sn—O bonds, the longer distance [2.939 (2) Å] is not representative of covalent Sn—O bonds. Such long bonds appear to be characteristic of bis[aquadiorgano(2,6-pyridinedicarboxylato)tin] complexes, and contrast with an average value of 2.0 Å found in dimeric tetrabutyldistannoxanes (Ng *et al.*, 1991).

(1)

Di-2-pyridylamine exists as a hydrogen-bonded dimer in two modifications: a low-melting polymorph and a high-melting polymorph. The pyridyl N atom is protonated in preference to the amino N atom, since
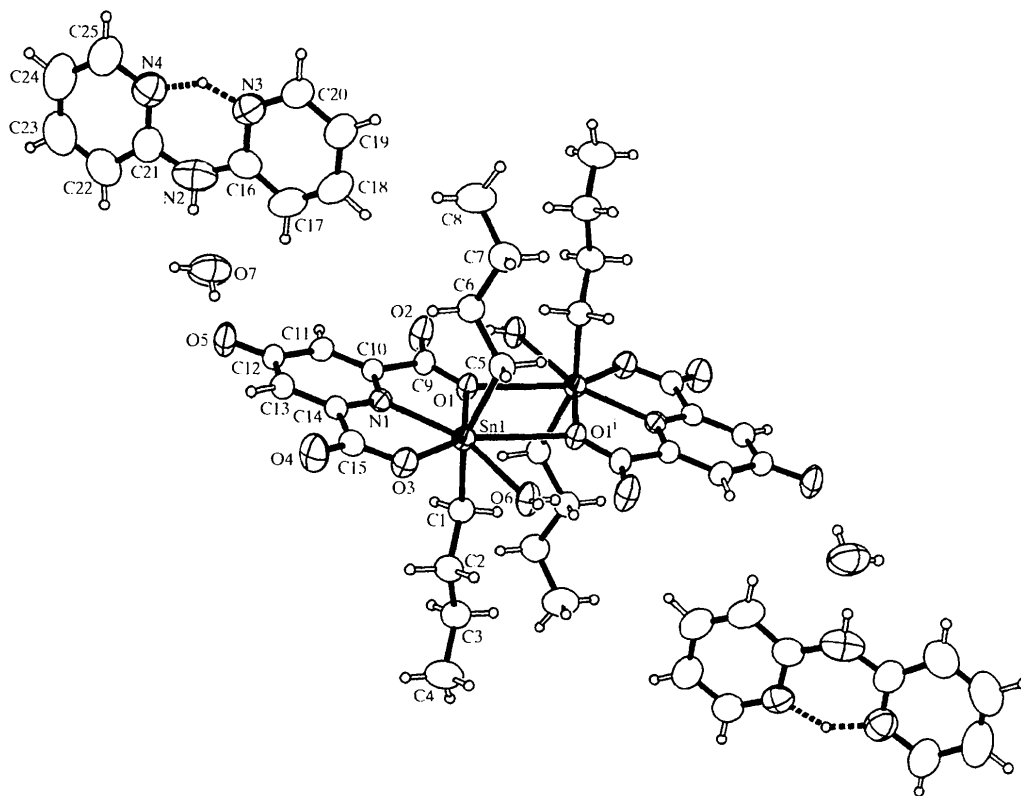
Fig. 1. *ORTEP*II (Johnson, 1976) plot at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

the pyridyl N atom is more basic, as implied by the formation of [2,2'-iminodipyridinium(1+)] tetraphenylborate and [2,2'-iminodipyridinium(1+)] hydrochloride dihydrate. The proton bridges the two pyridyl rings in the two salts; in the tetraphenylborate, the N···N interaction is 2.64 Å (N—H···N 143°; Gluth, 1993). The interaction is somewhat stronger in the organotin complex; the proton is 1.363 Å from the N3 atom and 1.342 Å from the N4 atom, which suggests an N···H···N description for the hydrogen-bonding scheme [N···N 2.592 (5) Å]. The two rings are coplanar [dihedral angle 3.3 (1)°]; they are twisted in the low-melting [dihedral angle 23°] and high-melting [dihedral angles of 7 and 29° in the two independent molecules] forms of the parent Lewis base (Johnson & Jacobson, 1973; Pyrka & Pinkerton, 1992).

The water molecule is linked by hydrogen bonds to the negatively charged hydroxy O [O···O 2.633 (4) Å], the carbonyl O [O···O 2.927 (5) Å] and amino N [O···N 2.810 (5) Å] atoms, and also to an adjacent water molecule [O···O 3.172 (8) Å]. The water–water interaction links the complex into a helical chain parallel to the b axis; in addition, the water–carbonyl O-atom interaction links the helices into wavy sheets. On the other hand, bis(diisopropylammonium) bis[aquadibutyl-(4-hydroxy-2,6-pyridinedicarboxylato)tin], which does not contain lattice water, adopts a one-dimensional

chain structure arising from N···O interactions only [N···O$_{hydroxyl}$ 2.719 (5) and N···O$_{esteryl}$ 2.954 (4) Å; Ng, 1998a].

Experimental

Di-2-pyridylamine, 4-hydroxy-2,6-pyridinedicarboxylic acid and dibutyltin oxide (2:2:1 molar ratio) were heated in ethanol until most of the solid had dissolved. The complex precipitated from the filtered solution as large crystalline blocks.

Crystal data

$(C_{10}H_{10}N_3)_2[Sn_2(C_7H_2NO_5)_2-$	Mo $K\alpha$ radiation
$(C_4H_9)_4(H_2O)_2].2H_2O$	$\lambda = 0.71073$ Å
$M_r = 1242.50$	Cell parameters from 25
Monoclinic	reflections
$P2_1/n$	$\theta = 12.0–13.0°$
$a = 9.226 (1)$ Å	$\mu = 1.032$ mm^{-1}
$b = 15.164 (2)$ Å	$T = 298 (2)$ K
$c = 18.868 (2)$ Å	Irregular block
$\beta = 99.03 (1)°$	$0.38 \times 0.38 \times 0.19$ mm
$V = 2606.9 (5)$ Å^3	Colorless
$Z = 2$	
$D_x = 1.583$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	3854 reflections with
diffractometer	$I > 2\sigma(I)$

ω scan
Absorption correction:
  ψ scan (North et al.,
  1968)
  $T_{min} = 0.729$, $T_{max} = 0.822$
10 063 measured reflections
4724 independent reflections

$R_{int} = 0.024$
$\theta_{max} = 25.69°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = -22 \rightarrow 22$
3 standard reflections
  frequency: 60 min
  intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 1.002$
4724 reflections
349 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 1.1434P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.846$ e Å^{-3}
$\Delta\rho_{min} = -0.402$ e Å^{-3}
Extinction correction: none
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)

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

Sn1—C1	2.114 (3)	Sn1—O1'	2.939 (2)
Sn1—C5	2.112 (3)	Sn1—O3	2.125 (2)
Sn1—N1	2.198 (2)	Sn1—O6	2.409 (2)
Sn1—O1	2.299 (2)		
C1—Sn1—C5	156.6 (1)	N1—Sn1—O1	69.2 (1)
C1—Sn1—N1	100.8 (1)	N1—Sn1—O1'	136.1 (1)
C1—Sn1—O1	86.3 (1)	N1—Sn1—O6	152.4 (1)
C1—Sn1—O1'	78.1 (1)	N1—Sn1—O3	72.0 (1)
C1—Sn1—O3	101.8 (1)	O1—Sn1—O1'	66.9 (1)
C1—Sn1—O6	83.1 (1)	O1—Sn1—O3	141.2 (1)
C5—Sn1—N1	99.2 (1)	O1—Sn1—O6	138.4 (1)
C5—Sn1—O1	89.4 (1)	O1'—Sn1—O3	151.8 (1)
C5—Sn1—O1'	79.0 (1)	O1'—Sn1—O6	71.5 (1)
C5—Sn1—O3	95.9 (1)	O3—Sn1—O6	80.4 (1)
C5—Sn1—O6	84.9 (1)		

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

A riding model was used to refine the H atoms, with $U(H) = 1.5U_{eq}(C)$. The water H atoms were located and refined with $U = 0.05$ Å^2. The pyridinium H atom is disordered between the N3 and N4 atoms, and was refined as one H atom with $U = 0.05$ Å^2.

Data collection: *CAD-4/PC* (Kretschmar, 1994). Cell refinement: *CELDIM* in *CAD-4 VAX/PC* (Enraf-Nonius, 1988). Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1200). Services for accessing these data are described at the back of the journal.

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Bis(3,5-dimethylpyrazole-N^2)(2,2-dimethyl-N-salicylideneglycinato-O,N,O')copper(II)

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Abstract

In the title compound, $[Cu(C_{11}H_{11}NO_3)(C_5H_8N_2)_2]$, the Cu^{II} atom adopts a square-pyramidal coordination, with a tridentate 2,2-dimethyl-N-salicylideneglycinate Schiff base dianion and a 3,5-dimethylpyrazole ligand bound in the basal plane. The apex of the elongated pyramid is occupied by a second 3,5-dimethylpyrazole molecule, with a Cu—N distance of 2.461 (2) Å. All molecules are arranged in a single magnetic orientation.

Comment

Owing to the diversity of resulting structures, copper(II) complexes with tridentate Schiff base dianions of the N-salicylideneaminoacidato type (TSB^{2-}) present a suitable model for the elucidation of structural and spectroscopic correlations. We are interested in the effect of the copper coordination, the Jahn–Teller distortion