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Outer-Sphere Coordination of a Multidentate *N*-Heterocycle to Tin Through Water: Monoclinic and Triclinic Modifications of *μ*-Succinato-bis(aquatriphenyltin)–2,4,6-Tris(2-pyridyl)-1,3,5-triazine (1/2)

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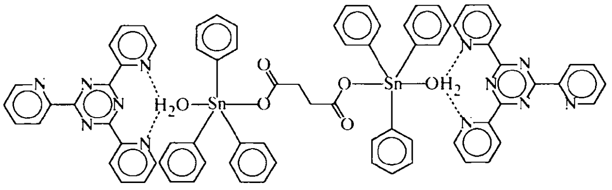
Abstract

The monoclinic and triclinic modifications of the title compound, $[\mathrm{Sn_2(C_4H_4O_4)(C_6H_5)_6(H_2O)_2}].2\mathrm{C_{18}H_{12}N_6}$, consist of a centrosymmetric bis(aquatriphenyltin) succinate complex, each coordinated water molecule of which is hydrogen bonded to two of the three pyridyl N atoms of a 2,4,6-tris(2-pyridyl)-1,3,5-triazine molecule.

Comment

Unlike most triphenyltin alkanoates that auto-associate through carboxylate bridges to form linear polymers having five-coordinate Sn atoms in *trans*-$\mathrm{C_3SnO_2}$ trigonal-bipyramidal geometries (Ng *et al.*, 1989; Tiekink, 1991, 1994), bis(triphenyltin) succinate exists as a tetrahedral molecule. This compound forms complexes with a number of monodentate *O*-donor ligands (Ng, 1998*a*) and the succinatotriphenylstannate polyanion has been isolated as its dicyclohexylammonium salt (Ng *et al.*, 1991). The Lewis acidity of bis(triphenyltin) succinate parallels that of triphenyltin trifluoroacetate, the Lewis acidity of which is ascribed to the electron-withdrawing trifluoroacetato group, as shown by the isolation of the bis(trifluoroacetato)triphenylstannate anion as the tetramethylammonium (Ng & Kumar Das, 1997) and pyridyl-2-amino-2-pyridinium (Ng, 1998*b*) salts. Triphenyltin trifluoroacetate furnishes a dimeric complex with 1,10-phenanthroline in which the heterocyclic ligand is attached indirectly, through the coordinated water molecule, to the metal atom [Sn—$\mathrm{O_{water}}$ 2.335 (4) Å]. The water molecule is hydrogen bonded to the N atom of one *N*-donor ligand as well as to the N atom of the centrosymmetrically related unit [O···N 2.809 (6) and 2.814 (6) Å; Ng *et al.*, 1996]. An attempt to prepare the analogous water-coordinated complex of 1,10-phenanthroline with bis(triphenyltin) succinate returned the starting reagents. Curiously, the multidentate *N*-heterocycle 2,4,6-tris(2-pyridyl)-1,3,5-triazine associates with bis(triphenyltin) succinate; however, the ligand uses only two of its three pyridyl groups to bind to a coordinated water molecule in the centrosymmetric complex *μ*-succinato-bis(aquatriphenyltin)–2,4,6-tris(2-pyridyl)-1,3,5-triazine (1/2), which crystallizes in monoclinic, (I), and triclinic, (II), modifications.



(I), (II)

The Sn atom in both modifications is five-coordinate; each Sn atom has the *trans*-$\mathrm{C_3SnO_2}$ trigonal-bipyramidal geometry in which the carboxyl and water O atoms occupy the axial sites and the *ipso*-C atoms of the phenyl rings the equatorial sites [monoclinic: Sn—O 2.115 (3) and 2.487 (3) Å, O—Sn—O 173.1 (1) and $\Sigma_{\mathrm{C—Sn—C}}$ 355.3 (6)°; triclinic: Sn—O 2.113 (3) and 2.441 (3) Å, O—Sn—O 175.3 (1) and $\Sigma_{\mathrm{C—Sn—C}}$ 356.8 (6)°]. In the monoclinic modification, one C—Sn—C angle is more compressed whereas another is opened up relative to the idealized value of 120° [C—Sn—C 107.8 (2), 116.2 (2) and 130.9 (2)°]; the angles in the triclinic modification show a smaller variation [115.2 (2), 119.0 (2) and 122.6 (2)°].

Triphenyltin chloride forms a monomeric aqua complex [Sn—O 2.317 (2) Å] with 2,2′:6′,2″-terpyridyl in which the water molecule forms hydrogen bonds to the pyridyl rings flanking the central pyridine moiety of terpyridyl [N···H···O 2.766 (2) and 2.807 (2) Å]; the interaction with the N atom of this moiety [N···O 2.949 (3) Å] is not regarded as a hydrogen bond as the three pyridyl rings of the terpyridyl ligand are twisted [dihedral angles 14.3 (3) and 32.0 (2)°; Prasad *et al.*, 1982]. The analogous isothiocyanate shows similar values [Sn—O 2.252 (2) Å, N···H···O 2.756 (3) and 2.798 (3) Å; dihedral angles 19.6 (3) and 29.5 (3)°], and the interaction between water and the central pyridyl N atom is similarly discounted (Prasad & Smith, 1982), as is that found in the triphenyltin chloride complex with 3-(1,10-phenanthrolin-2-yl)-5,6-diphenyl-1,2,4-triazine, in which the phenanthrolinyl portion of the *N*-heterocycle is flat (Ladd *et al.*, 1982). In the bis(triphenyltin) succinate complex, the three pyridyl rings are twisted relative to the triazine ring [dihedral angles in the mono-

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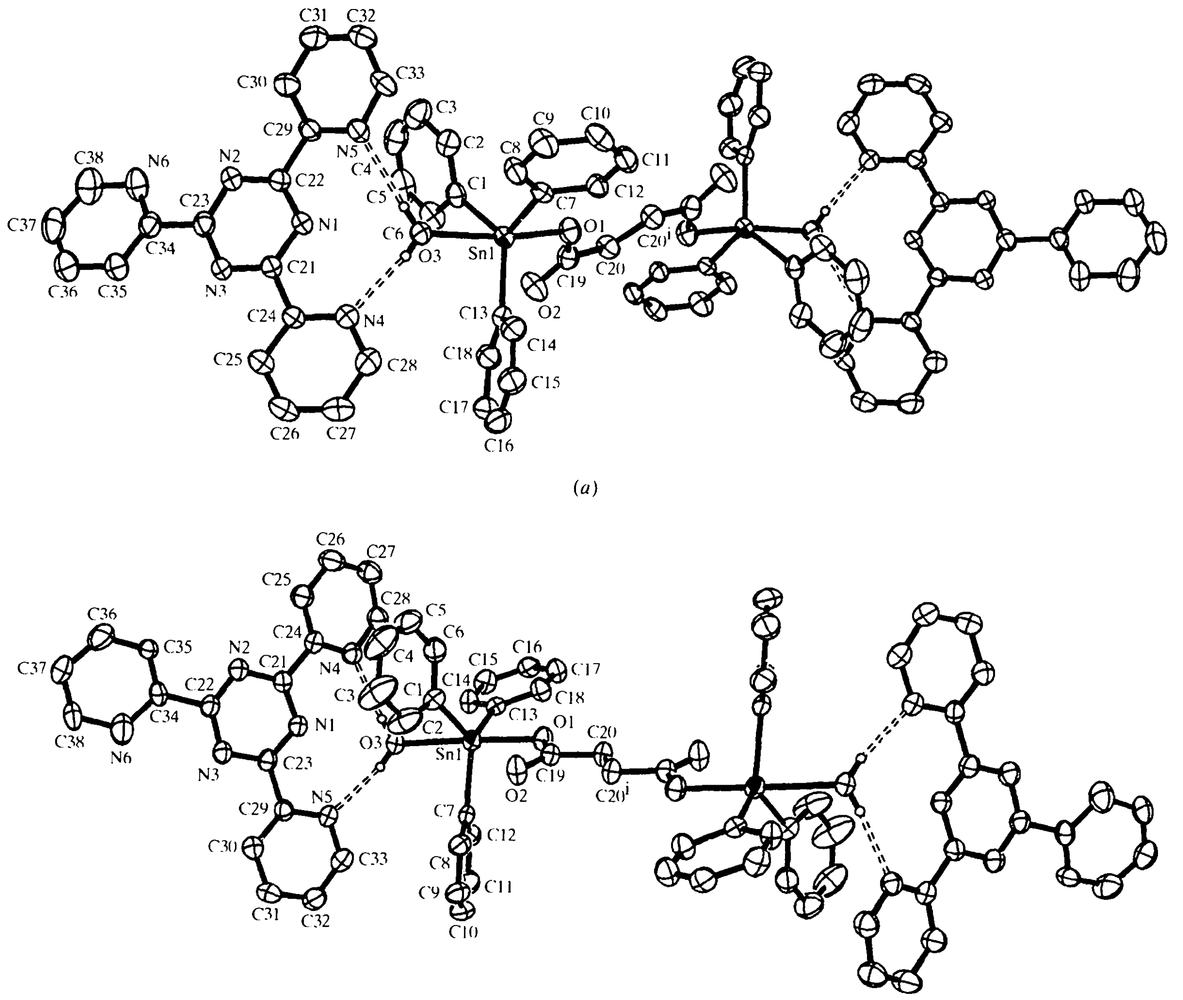

(a)

(b)

Fig. 1. *ORTEPII* (Johnson, 1976) plots of (*a*) the monoclinic modification, (I), and (*b*) the triclinic modification, (II), at the 40% probability level. Only water H atoms are shown, represented as spheres of arbitrary radii.

clinic modification: 8.5 (2), 8.6 (2) and 12.6 (3)°; dihedral angles in the triclinic modification: 1.5 (3), 12.3 (3) and 18.8 (2)°]. The rings are more twisted in the parent Lewis base (Drew *et al.*, 1998).

The monoclinic modification has no solvent-accessible voids whereas there are two voids of 39.2 Å^3 in the unit cell of the triclinic modification, as calculated by *PLATON* (Spek, 1990), but the voids do not abut any O or N atoms (*cf.* a hydrogen-bonded water molecule occupies about 40 Å^3).

Experimental

Bis(triphenyltin) succinate was prepared by treating triphenyltin hydroxide with succinic acid in ethyl acetate (Ng, 1998*a*). The organotin carboxylate was heated with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (1:1 molar ratio) in a small volume of ethyl acetate. On slow evaporation of the solvent, the filtered solution yielded two types of crystals, *i.e.* long colorless plates and tan-colored 'rose-rock' crystals. A 'petal' of the rose rock was cut into a wavy plate for the diffraction measurements; the compound was identified as the monoclinic modification, (I). The triclinic modification, (II), was obtained when the reaction was carried out with ethanol as solvent. The product when recrystallized from ethanol also yielded colorless plates and tan blocks. A regular-shaped tan specimen was used for the measurements. The colorless plates that were formed in both reactions were identified as bis(triphenyltin) succinate from its cell constants.

Compound (I) (monoclinic modification)

Crystal data

$[Sn_2(C_4H_4O_4)(C_6H_5)_6(H_2O)_2].2C_{18}H_{12}N_6$
$M_r = 1476.76$
Monoclinic
$P2_1/a$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.0–13.0°$

$a = 8.1259\ (6)$ Å
$b = 32.017\ (2)$ Å
$c = 13.011\ (1)$ Å
$\beta = 103.065\ (7)°$
$V = 3297.5\ (4)$ Å^3
$Z = 2$
$D_x = 1.487$ Mg m^{-3}
D_m not measured

$\mu = 0.823$ mm^{-1}
$T = 298\ (2)$ K
Block
$0.36 \times 0.32 \times 0.28$ mm
Light tan

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scan
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.719$, $T_{max} = 0.794$
6232 measured reflections
5796 independent reflections

4082 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 24.98°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 38$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.085$
$S = 0.990$
5796 reflections
440 parameters
H atoms riding, $U(\mathrm{H}) = 1.5U_{eq}(\mathrm{C})$; water H atoms located and refined with common U_{iso}

$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.8346P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.425$ e Å^{-3}
$\Delta\rho_{min} = -0.294$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sn1—C1	2.128 (4)	Sn1—O3	2.487 (3)
Sn1—C7	2.134 (4)	O3···N4	2.921 (5)
Sn1—C13	2.133 (4)	O3···N5	2.999 (5)
Sn1—O1	2.115 (3)		
C1—Sn1—C7	116.6 (2)	C7—Sn1—O1	90.6 (1)
C1—Sn1—C13	130.9 (2)	C7—Sn1—O3	87.8 (1)
C1—Sn1—O1	94.5 (1)	C13—Sn1—O1	105.4 (1)
C1—Sn1—O3	80.2 (1)	C13—Sn1—O3	81.5 (1)
C7—Sn1—C13	107.8 (2)	O1—Sn1—O3	173.1 (1)

Compound (II) (triclinic modification)

Crystal data

$[Sn_2(C_4H_4O_4)(C_6H_5)_6(H_2O)_2].2C_{18}H_{12}N_6$
$M_r = 1476.76$
Triclinic
$P\overline{1}$
$a = 9.2219\ (8)$ Å
$b = 12.567\ (2)$ Å
$c = 15.616\ (2)$ Å
$\alpha = 78.73\ (1)°$
$\beta = 73.681\ (9)°$
$\gamma = 80.395\ (9)°$
$V = 1691.3\ (3)$ Å^3
$Z = 1$
$D_x = 1.450$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.0–11.0°$
$\mu = 0.802$ mm^{-1}
$T = 298\ (2)$ K
Irregular plate
$0.40 \times 0.40 \times 0.10$ mm
Light tan

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.847$, $T_{max} = 0.923$
6327 measured reflections
5908 independent reflections

4767 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.095$
$S = 1.016$
5908 reflections
440 parameters
H atoms riding, $U(\mathrm{H}) = 1.5U_{eq}(\mathrm{C})$; water H atoms located and refined with common U_{iso}

$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.1970P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.476$ e Å^{-3}
$\Delta\rho_{min} = -0.386$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

Sn1—C1	2.125 (4)	Sn1—O3	2.441 (3)
Sn1—C7	2.129 (4)	O3···N4	2.860 (5)
Sn1—C13	2.143 (4)	O3···N5	2.907 (5)
Sn1—O1	2.133 (3)		
C1—Sn1—C7	122.6 (2)	C7—Sn1—O1	96.5 (1)
C1—Sn1—C13	119.0 (2)	C7—Sn1—O3	82.1 (1)
C1—Sn1—O1	100.5 (1)	C13—Sn1—O1	90.2 (1)
C1—Sn1—O3	83.9 (1)	C13—Sn1—O3	86.3 (1)
C7—Sn1—C13	115.2 (2)	O1—Sn1—O3	175.3 (1)

For both compounds, data collection: *CAD-4/PC* (Kretschmar, 1994); cell refinement: *CELDIM* in *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988); data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *ORTEP*II (Johnson, 1976); 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: SK1192). Services for accessing these data are described at the back of the journal.

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Metallo-Ligand $[Cu^{II}(carboxylato)_4]^{2+}$ Cores: Tetrakis(trimethylammonioacetato-*O*)copper Diperchlorate and its 1/1 Complex with Sodium Perchlorate

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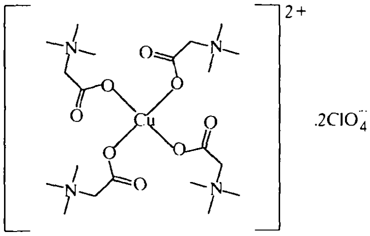
Abstract

The crystal structure of tetrakis(trimethylammonioacetato-*O*)copper diperchlorate, $[Cu(C_5H_{11}NO_2)_4](ClO_4)_2$, consists of discrete $[Cu\{(CH_3)_3NCH_2CO_2\}_4]^{2+}$ cations and ClO_4^- anions. The Cu atom is coordinated by four trimethylammonioacetate ligands in a square-planar geometry. The compound forms a 1/1 complex with sodium perchlorate, *i.e.* perchlorato-2κ*O*-bis(μ-trimethylammonioacetato)-1:2κ^4*O*-bis(trimethylammonioacetato)-1κ^2*O*-coppersodium diperchlorate, $[Cu(C_5H_{11}NO_2)_4\{Na(ClO_4)\}](ClO_4)_2$, in which the Cu and Na atoms are bridged by either three μ_2-carboxylato-*O*,*O*′ or two μ_2-carboxylato-*O* groups to give rise to a linear cationic chain.

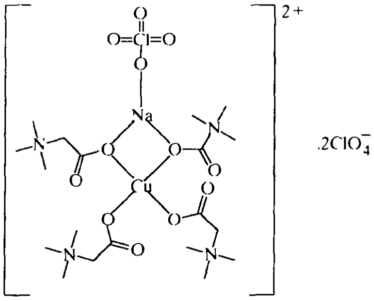
Comment

Four zwitterionic betaine molecules (or other betaine homologs) can be assembled around a Cu^{II} atom to provide a $[Cu(betaine)_4]^{2+}$ 'metallo-ligand' core that binds to hard metal ions such as Li^I, Ca^{II} and La^{III} ions through the carboxyl oxygen ends (Chen & Mak, 1994*a*,*b*; Wu *et al.*, 1995). The charges of the cation are typically balanced by perchlorate anions, such anions being chosen because of their lack of Lewis basicity, and several octadecanuclear copper–lanthanoid clusters have been synthesized. Interestingly, their crystal structures reveal the presence of an encapsulated perchlorate ion (Chen *et al.*, 1995, 1996). The tetrakis(trimethylammonioacetato-*O*)copper perchlorate homolog itself has not been crystallographically examined, although the metallo-ligand core has been authenticated in the nitrate (Chen & Mak, 1991).

The crystal structure of tetrakis(trimethylammonioacetato-*O*)copper diperchlorate, (I), consists of discrete $[Cu\{(CH_3)_3NCH_2CO_2\}_4]^{2+}$ cations and ClO_4^- anions.



(I)



(II)

The Cu atom occupies the Wyckoff position 2*a* (point symmetry: $\bar{4}2m$ or *D2d*) and is coordinated by four trimethylammonioacetate ligands. The Cu atom shows almost idealized square-planar coordination [Cu—O = 1.948 (2) Å; O—Cu—O_{cis} = 90.0 (1) and O—Cu—O_{trans} = 177.5 (3)°]. The four double-bonded O atoms point into the square plane [Cu···O = 2.906 (4) Å], so that the ligands complex to the metal atom in an up/down–up/down–up/down–up/down fashion, if the Cu···O interaction is regarded as a weak bond (Fig. 1). The coordination environment of the Cu atom in (I) is similar to that of the Cu atom in tetrakis(trimethylammonioacetato-*O*)copper nitrate [Cu—O = 1.948 (3) and Cu···O = 2.833 (3) Å; Chen & Mak, 1991]. The

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