For the iron complex, the temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). For the copper complex, the data collection nominally covered over a hemisphere of reciprocal space by a combination of several sets of exposures. Information on percentage coverage is not available. Crystal decay was found to be negligible by analysing duplicate reflections.

H atoms were added at calculated positions (except as noted below) and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms (except as noted below); H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the carrier atom. In compound (1), the central C atom of the macrocyclic ring is disordered; the two C atoms and the two sets of idealized H atoms attached to C1–C3 were refined with linked occupancies [the refined occupancy for the major component was 0.69 (1)]. Although the largest residual Fourier peaks are considerably less than 1 e Å^{-3} in height, they are located in a large void in the unit cell (160 Å^3) and may indicate the presence of extremely disordered solvent. Compound (2) has two independent cations, four anions and one molecule of acetonitrile in the asymmetric unit. Cation *A* has two disordered CH_2 groups, C13*A/B* and C11*A/B* [with very similar occupancies, refined together as 0.719 (2):0.281 (2)]. Cation *B* is highly disordered and atoms C22–C24 [occupancies 0.55 (2):0.45 (2)], C26–C28 [0.66 (2):0.34 (2)] and C210–C212 [0.51 (2):0.49 (2)] were all refined as disordered pairs. Only the H atoms of the major components of cation *A* and the non-disordered atoms of cation *B* were included. The second and third $[PF_6]^-$ anions were also modelled with four equatorial F atoms doubled. All P— F and F⋯F distances were restrained [refined P—F value = 1.549 (3) Å]. Anisotropic displacement parameters were not used for the minor components of cation *A*, the disordered atoms of cation *B* and some of the disordered F atoms. High displacement parameters for some other F atoms suggest additional unmodelled disorder.

Data collection: *R3M* (Siemens, 1986) for (1); *MADNES* (Pflugrath & Messerschmidt, 1992) for (2). Cell refinement: *R3M* for (1); *MADNES* for (2). Data reduction: *R3M* for (1); *MADNES* for (2). Program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990a) for (1); *SHELXS86* (Sheldrick, 1990b) for (2). Program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997) for (1); *SHELXL93* (Sheldrick, 1993) for (2). Molecular graphics: *XP* (Siemens, 1995) for (1); *SHELXTL-Plus* for (2). Software used to prepare material for publication: *XCIF* for (1); *SHELXTL-Plus* for (2).

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Triphenyltin N,N-dimethylthiocarbamoylacetate, triphenyltin N,N-pentamethylenecarbamoylthioacetate and cyclopentyldiphenyltin N,N-dimethylthiocarbamoylacetate

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@cc.um.edu.my*

Abstract

Carboxylate bridges link two independent molecules of triphenyltin N,N-dimethylthiocarbamoylacetate, [Sn-$(C_6H_5)_3(C_5H_8NO_3S)$], into a helical chain {*i.e. catena*-poly[triphenyltin-μ-(N,N-dimethylthiocarbamoylacetato-O:O')]}, as do the carboxylate bridges in triphenyltin N,N-pentamethylenecarbamoylthioacetate, [Sn(C_6H_5)_3-$(C_8H_{12}NO_3S)$] {*i.e. catena*-poly[triphenyltin-μ-(N,N-

pentamethylenethiocarbamoylacetato-O:O')]}, and cyclopentyldiphenyltin N,N-dimethylthiocarbamoylacetate, [Sn(C₆H₅)₂(C₅H₉)(C₅H₈NO₃S)] {*i.e.* catena-poly[cyclopentyldiphenyltin-μ-(N,N-dimethylthiocarbamoylacetato-O:O')]}.

Comment

Triphenyltin N,N-dimethylthiocarbamoylthio-S-acetate, [(C₆H₅)₃SnO₂CCH₂SC(S)N(CH₃)₂], crystallizes as two independent molecules that are linked by carboxylate bridges [2.307 (9) and 2.315 (8) Å] into a helical chain along **b** (Ng & Kumar Das, 1995). Triphenyltin N,N-dimethylthiocarbamoyl-O-acetate, (I), which exhibits comparable fungicidal activity (Kumar Das *et al.*, 1989), is isostructural; both compounds have matching unit-cell dimensions and atomic coordinates. The carboxylate bridges in the present compound, (I) [2.314 (3) and 2.352 (3) Å], are not statistically different. Bond dimensions involving the carboxylate anion are similar to those of the parent acid, (CH₃)₂NC(S)OCH₂CO₂H (Ng, 1993). The carboxylate-bridged architecture differs from the hydrogen-bonded chain structure adopted by the triphenyltin 3-oxapentamethylenethiocarbamoylacetate derivative, which crystallizes as a water-coordinated dinuclear monohydrate, [(C₆H₅)₃SnO₂CCH₂OC(S)N(CH₂CH₂)₂O]₂·H₂O (Ng, 1996).

effect of the larger substituent is reflected in a large void in the crystal structure. On the other hand, solvent-accessible voids are absent in cyclopentyldiphenyltin N,N-dimethylthiocarbamoylacetate, (III), which also adopts a carboxylate-bridged [2.344 (6) and 2.395 (5) Å] structure. The three compounds propagate by twofold screw-axial translations along the *b* axis of their unit cells; the repeat distance of these polymer chains, which

(a)

(I)

(II)   (III)
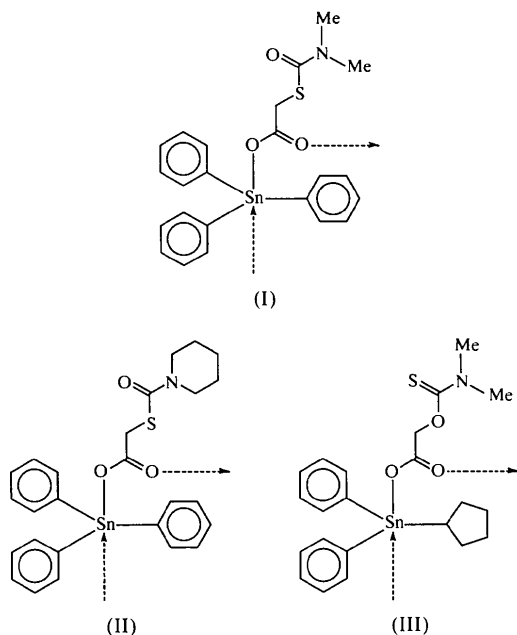
The triphenyltin N,N-pentamethylenecarbamoylthio-acetate, (II), which has a somewhat larger substituent in the anionic group, displays a similar carboxylate-bridged [2.323 (5) and 2.333 (4) Å] chain structure. The
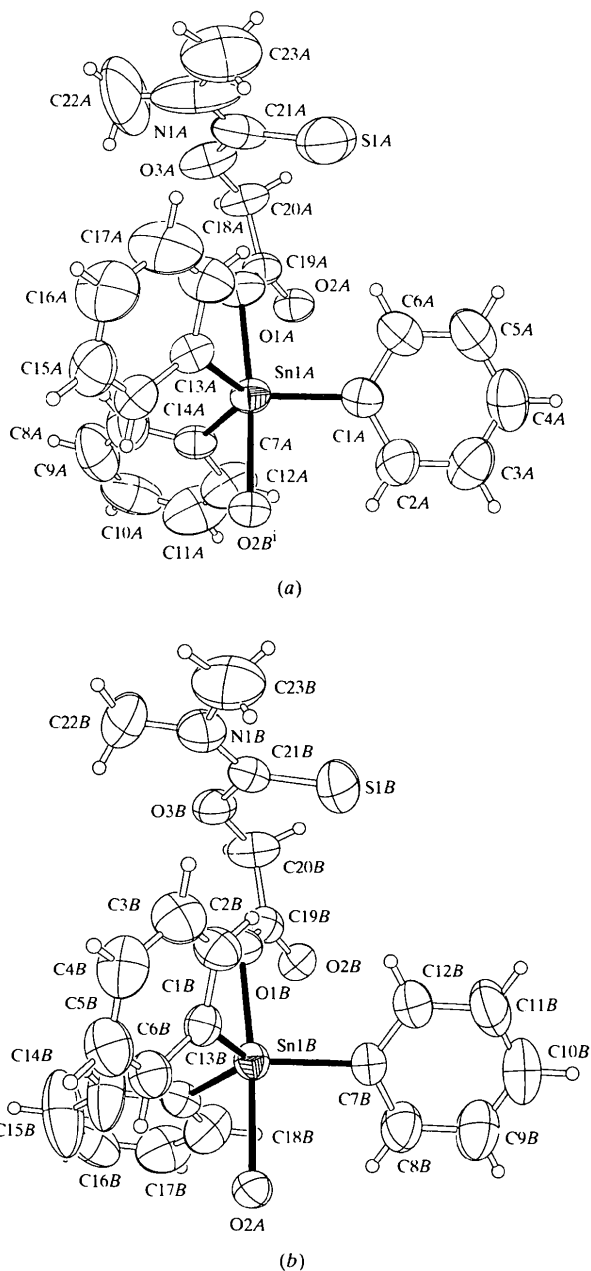
(b)

Fig. 1. *ORTEP*II (Johnson, 1976) plot of (a) molecule A and (b) molecule B of (I), showing displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

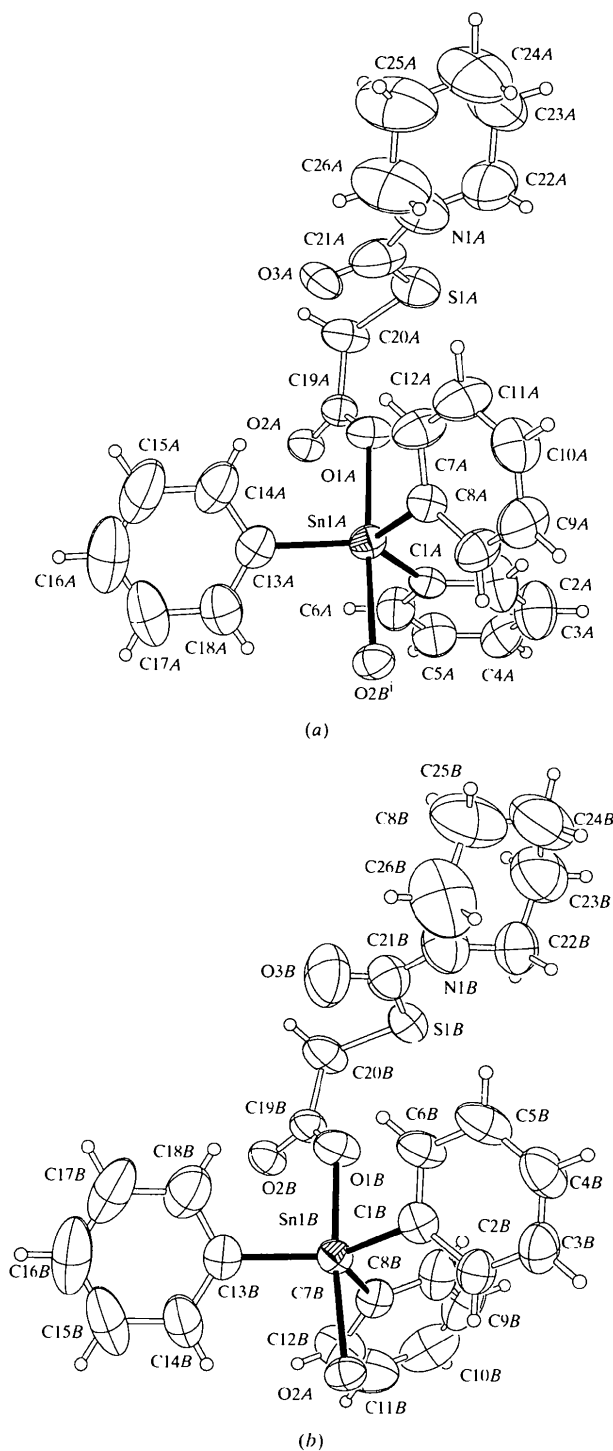is b/2, is shorter than the repeat distance of most carboxylate-bridged triorganotin carboxylates (Ng *et al.*, 1988).

Fig. 2. *ORTEP*II (Johnson, 1976) plot of (a) molecule A and (b) molecule B of (II), showing displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Fig. 3. *ORTEP*II (Johnson, 1976) plot of (a) molecule A and (b) molecule B of (III), showing displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.
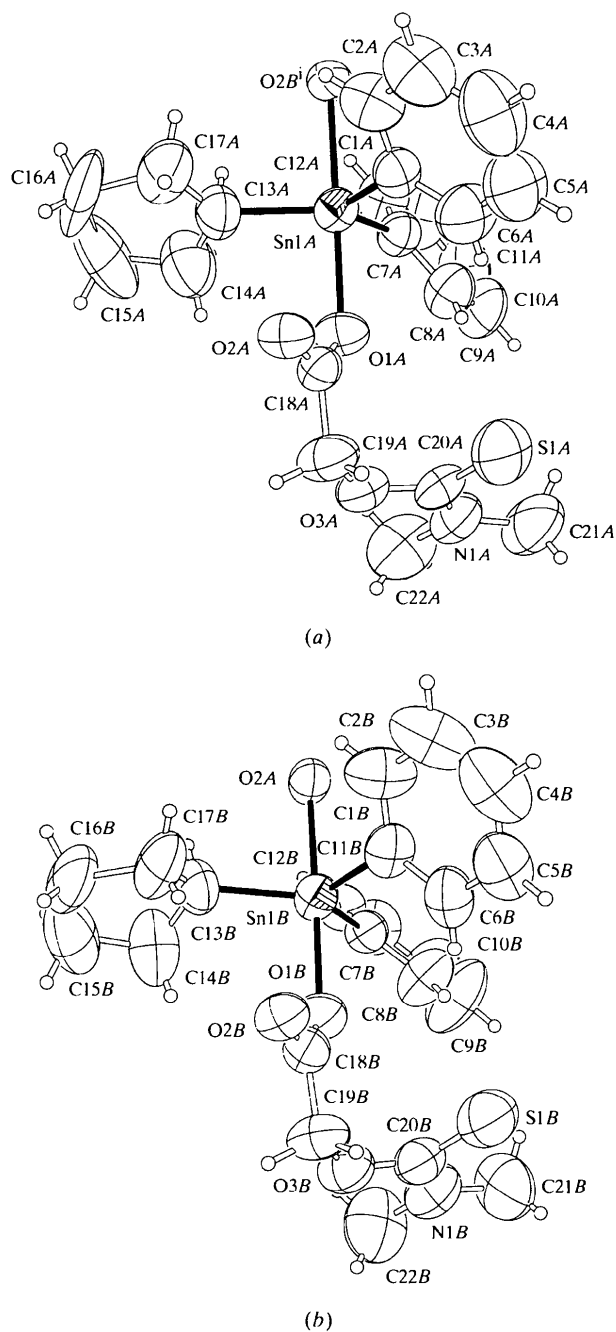
Experimental

Sodium glycolate, NaO_2CCH_2OH, was treated with carbon disulfide to give the xanthate, $Na_2(O_2CCH_2OCS_2)$, which was used to displace the chloride from chloroacetamide to furnish the sodium salt of S-carbamylmethyl-2-(carboxylethyl)xanthic acid, $HO_2CCH_2OCS_2CH_2C(O)NH_2$. This xanthic acid, when

aminolysed with dimethylamine, yielded N,N-dimethylthio-carbamoylacetic acid (Pluijgers, 1959; Pluijgers & van der Kerk, 1961). Equimolar quantities of the acetic acid and triphenyltin hydroxide were heated in a small volume of ethanol; (I) separated on cooling the filtered solution. Potassium penta-methylenemonothiocarbamate, KSC(O)N(CH₂)₅, was obtained from the reaction between carbonyl sulfide and piperidine. The salt was used to displace chloride from chloroacetic acid (Pluijgers, 1959) to afford N,N-pentamethylenecarbamoylthio-acetic acid. The condensation between equimolar amounts of this acid and triphenyltin hydroxide in ethanol yielded (II). The synthesis of (III) required cyclopentyldiphenyltin hydroxide. Cyclopentyltriphenyltin was prepared from the Grignard reaction between cyclopentylmagnesium bromide and triphenyltin chloride; one of its phenyl groups was cleaved by bromide to give cyclopentyldiphenyltin bromide, which was then hydrolysed to the hydroxide. The method for the preparation of the bromide was that used for preparing butyl-diphenyltin bromide (Kumar Das et al., 1982). The hydroxide, when condensed with N,N-dimethylthiocarbamoylacetic acid, yielded (III).

Compound (I)

Crystal data

[Sn(C₆H₅)₃(C₅H₈NO₃S)]
$M_r = 512.17$
Monoclinic
$P2_1/c$
$a = 12.193\,(1)$ Å
$b = 17.562\,(2)$ Å
$c = 21.840\,(3)$ Å
$\beta = 97.71\,(1)°$
$V = 4634.5\,(9)$ Å³
$Z = 8$
$D_x = 1.468$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–13°$
$\mu = 1.215$ mm⁻¹
$T = 298\,(2)$ K
Block
$0.55 \times 0.50 \times 0.45$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction:
 ψ scan (North et al., 1968)
 $T_{min} = 0.509$, $T_{max} = 0.579$
8547 measured reflections
8138 independent reflections
5931 reflections with
 $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 24.98°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = -25 \rightarrow 25$
3 standard reflections
 frequency: 60 min
 intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.108$
$S = 1.018$
8138 reflections
451 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 4.1675P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.937$ e Å⁻³
$\Delta\rho_{min} = -0.631$ e Å⁻³
Extinction correction: none
Scattering factors from
 International Tables for Crystallography (Vol. C)

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

Sn1A—C1A	2.122 (3)	Sn1B—C1B	2.138 (2)
Sn1A—C7A	2.112 (3)	Sn1B—C7B	2.130 (3)
Sn1A—C13A	2.130 (2)	Sn1B—C13B	2.116 (3)
Sn1A—O1A	2.193 (3)	Sn1B—O1B	2.204 (3)
Sn1A—O2B'	2.314 (3)	Sn1B—O2A	2.352 (3)
C1A—Sn1A—C7A	119.4 (2)	C1B—Sn1B—C7B	118.9 (1)
C1A—Sn1A—C13A	121.5 (1)	C1B—Sn1B—C13B	118.1 (1)
C1A—Sn1A—O1A	95.9 (2)	C1B—Sn1B—O1B	86.3 (1)
C1A—Sn1A—O2B'	90.0 (1)	C1B—Sn1B—O2A	89.0 (1)
C7A—Sn1A—C13A	118.9 (2)	C7B—Sn1B—C13B	122.7 (1)
C7A—Sn1A—O1A	93.2 (1)	C7B—Sn1B—O1B	95.1 (1)
C7A—Sn1A—O2B'	87.7 (1)	C7B—Sn1B—O2A	90.2 (1)
C13A—Sn1A—O1A	85.7 (1)	C13B—Sn1B—O1B	93.6 (1)
C13A—Sn1A—O2B'	87.5 (1)	C13B—Sn1B—O2A	85.7 (1)
O1A—Sn1A—O2B'	172.7 (1)	O1B—Sn1B—O2A	174.2 (1)
C19A—O1A—Sn1A	128.8 (3)	C19B—O1B—Sn1B	124.4 (3)
C19B—O2B—Sn1Aⁱⁱ	135.0 (3)	C19A—O2A—Sn1B	139.3 (3)

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

Compound (II)

Crystal data

[Sn(C₆H₅)₃(C₈H₁₂NO₃S)]
$M_r = 552.24$
Monoclinic
$C2/c$
$a = 27.404\,(1)$ Å
$b = 17.855\,(1)$ Å
$c = 21.682\,(1)$ Å
$\beta = 98.11\,(1)°$
$V = 10502.1\,(9)$ Å³
$Z = 16$
$D_x = 1.397$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.5–13.0°$
$\mu = 1.078$ mm⁻¹
$T = 298\,(2)$ K
Block
$0.29 \times 0.29 \times 0.22$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
 ψ scan (North et al., 1968)
 $T_{min} = 0.724$, $T_{max} = 0.789$
9424 measured reflections
9222 independent reflections
6114 reflections with
 $I > 2\sigma(I)$

$R_{int} = 0.027$
$\theta_{max} = 24.98°$
$h = 0 \rightarrow 32$
$k = -21 \rightarrow 0$
$l = -25 \rightarrow 25$
3 standard reflections
 frequency: 60 min
 intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.169$
$S = 1.095$
9236 reflections
505 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0905P)^2 + 12.9988P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.414$ e Å⁻³
$\Delta\rho_{min} = -0.715$ e Å⁻³
Extinction correction: none
Scattering factors from
 International Tables for Crystallography (Vol. C)

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

Sn1A—C1A	2.114 (4)	Sn1B—C1B	2.139 (3)
Sn1A—C7A	2.141 (3)	Sn1B—C7B	2.110 (4)
Sn1A—C13A	2.132 (4)	Sn1B—C13B	2.120 (4)

Sn1A—O1A	2.201 (5)	Sn1B—O1B	2.188 (5)
Sn1A—O2B'	2.323 (5)	Sn1B—O2A	2.333 (4)
C1A—Sn1A—C7A	116.9 (2)	C1B—Sn1B—C7B	113.9 (2)
C1A—Sn1A—C13A	123.2 (2)	C1B—Sn1B—C13B	123.6 (2)
C1A—Sn1A—O1A	96.2 (2)	C1B—Sn1B—O1B	85.9 (2)
C1A—Sn1A—O2B'	83.4 (2)	C1B—Sn1B—O2A	87.9 (2)
C7A—Sn1A—C13A	119.5 (2)	C7B—Sn1B—C13B	122.2 (2)
C7A—Sn1A—O1A	86.5 (2)	C7B—Sn1B—O1B	95.1 (2)
C7A—Sn1A—O2B'	90.4 (2)	C7B—Sn1B—O2A	85.8 (2)
C13A—Sn1A—O1A	93.1 (2)	C13B—Sn1B—O1B	94.7 (2)
C13A—Sn1A—O2B'	90.2 (2)	C13B—Sn1B—O2A	90.4 (2)
O1A—Sn1A—O2B'	176.3 (2)	O1B—Sn1B—O2A	173.5 (2)
C19A—O1A—Sn1A	128.2 (4)	C19B—O1B—Sn1B	128.6 (5)
C19A—O2A—Sn1B	134.9 (4)	C19B—O2B—Sn1A"	139.6 (4)

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

Compound (III)

Crystal data

[Sn(C$_6$H$_5$)$_2$(C$_5$H$_9$)-
(C$_5$H$_8$NO$_3$S)]
M_r = 504.20
Monoclinic
$P2_1/c$
a = 12.307 (2) Å
b = 17.528 (2) Å
c = 21.781 (4) Å
β = 97.77 (1)°
V = 4656 (1) Å^3
Z = 8
D_x = 1.439 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25
    reflections
θ = 14–16°
μ = 1.208 mm^{-1}
T = 298 (2) K
Block
0.40 × 0.35 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4
    diffractometer
$\omega/2\theta$ scans
Absorption correction:
    ψ scan (North et al.,
    1968)
    T_{min} = 0.430, T_{max} = 0.767
9449 measured reflections
8149 independent reflections
4611 reflections with
    $I > 2\sigma(I)$

R_{int} = 0.052
θ_{max} = 24.97°
h = 0 → 14
k = 0 → 20
l = −25 → 25
3 standard reflections
    frequency: 60 min
    intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.185
S = 1.049
8149 reflections
457 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.864 e Å^{-3}
$\Delta\rho_{min}$ = −1.328 e Å^{-3}
Extinction correction: none
Scattering factors from
    *International Tables for
    Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (III)*

Sn1A—C1A	2.113 (5)	Sn1B—C1B	2.142 (5)
Sn1A—C7A	2.139 (5)	Sn1B—C7B	2.136 (4)
Sn1A—C13A	2.068 (9)	Sn1B—C13B	2.119 (9)
Sn1A—O1A	2.187 (5)	Sn1B—O1B	2.202 (6)
Sn1A—O2B'	2.395 (5)	Sn1B—O2A	2.344 (6)
C1A—Sn1A—C7A	119.0 (3)	C1B—Sn1B—C7B	117.4 (2)
C1A—Sn1A—C13A	123.6 (3)	C1B—Sn1B—C13B	120.8 (3)
C1A—Sn1A—O1A	96.1 (2)	C1B—Sn1B—O1B	96.4 (3)

The phenyl rings were refined as rigid hexagons in the three structures. In (II), the final difference map had only one peak larger than 1 e Å^{-3}; this peak, at (0.016, 0.533, 0.241), is 3.46 Å from the H17B atom. A check with *PLATON* (Spek, 1990) showed that the unit cell has four solvent-accessible voids, each of 186 Å^3. One of the voids exists at (0, 0.564, 0.25). However, the electron density could not be refined as a disordered water molecule. The *SQUEEZE* option (van der Sluis & Spek, 1990) in *PLATON* was applied to the diffraction data. The C—C distances in the two N(CH$_2$)$_5$ rings were *DFIX*ed at 1.54±0.01 Å. In (III), the C—C distances of the cyclopentyl rings were *DFIX*ed at 1.54±0.01 Å. In the final difference map, the largest peak and hole are about 1 Å from the Sn1A atom. For (I), (II) and (III), H atoms were treated as riding, with U(H) = 1.5U_{eq}(C).

For all compounds, 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 structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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{4,4'-Dimethyl-6,6'-bis(1-morpholiniomethyl)-2,2'-[1,2-ethanediylbis(nitrilomethylidene-N)]diphenolato-O,O'}-copper(II) diperchlorate monohydrate

S. Shanmuga Sundara Raj,[a] R. Thirumurugan,[b] G. Shanmugam,[b] Hoong-Kun Fun,[a] J. Manonmani[c] and M. Kandaswamy[c]

[a]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia,* [b]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and* [c]*Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India. E-mail: hkfun@usm.my*

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Abstract

The crystal structure of the title compound, [Cu(C$_{28}$H$_{38}$N$_4$O$_4$)](ClO$_4$)$_2$·H$_2$O, shows that the Cu^{II} ion is in a distorted square-pyramidal environment. The average Cu—O and Cu—N bond lengths are 1.916 (2) and 1.936 (3) Å, respectively. Both of the morpholino rings adopt a chair conformation. Even though enough chelating centres are available to coordinate more than one metal atom, because of the steric interaction of the morpholino rings only one Cu atom is coordinated to the ligand.

Comment

The function and properties of active sites in metal complexes are determined by the environment and coordination sites around the metal ion. Synthesis and structural studies of metal complexes should provide additional information on this issue. The mononuclear Cu site in the enzyme galactose oxidase is essential for catalysing a two-electron transfer reaction during the oxidation of primary alcohols to the corresponding aldehydes (Ito *et al.*, 1991). Galactose oxidase is unusual

among copper enzymes in participating in this catalysis of the two-electron redox chemistry of a mononuclear active site (Whittaker *et al.*, 1996). The study of metal complexes is focused very much towards the field of biomimicry, where they can be used as models for biological metallo-compounds, such as proteins and enzymes (Suzuki *et al.*, 1984). The present structural study of the title complex, (I), is the continuation of our previous work (Raj *et al.*, 1999).

(I)
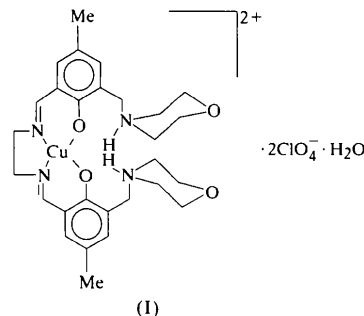
The O9 atom of the perchlorate ion coordinates with the Cu atom to make the metal pentacoordinate [Cu1···O9 2.832 (4) Å]. The Cu atom is in a distorted square-pyramidal environment, with the basal plane being defined by the two phenyloxy O atoms and the two imino N atoms. These O and N atoms extend the same type of coordination. The steric interaction of the morpholino rings restricts the coordination of a further metal atom in the other half of the complex, even though enough chelating centres are available (Kahn, 1982), where O1 and O4 can act as bridges. Due to steric interaction between the two bulky morpholino rings, the C2—C8—N1 [114.2 (2)°] and C21—C24—N4 [110.2 (2)°] angles are smaller than those of C6—C13—N2 [125.0 (3)°] and C17—C16—N3 [124.7 (3)°]. The bond lengths and angles in (I) are comparable with those of the ligand (Raj *et al.*, 1999). The five-membered ring, with Cu as one of the hetero atoms, is in a '*gauche*' conformation (Panneerselvam *et al.*, 1998) and the two six-membered rings are planar.

The decrease in the N2—Cu1—N3 angle [83.6 (1)°] may be due to the lack of macrocyclic closeness of the ligand. The N atoms of the morpholino rings are protonated and are involved in N—H···O hydrogen bonding. The morpholino rings adopt a chair conformation. The best plane passes through the central C atoms, leaving the N and O atoms above and below the plane. The deviations of these N and O atoms are 0.640 (3) and −0.677 (3) Å, respectively, for the ring consisting of atoms C9–C12, N1 and O1, and 0.645 (3) and −0.683 (3) Å, respectively, for the ring consisting of atoms C25–C28, N4 and O4.

The two phenyl rings are coplanar, making a dihedral angle of 3.8 (1)°, and the morpholino rings make