

Table 1. Selected geometric parameters (Å, °)

| | | | |
|---------------|------------|---------------|------------|
| Cu—O23 | 1.891 (2) | Cu'—O21' | 1.896 (2) |
| Cu—O21 | 1.901 (2) | Cu'—N1' | 1.987 (2) |
| Cu—N1 | 1.993 (2) | Cu'—N10' | 1.995 (2) |
| Cu—N10 | 2.001 (2) | Cu'—O23 | 2.443 (3) |
| Cu—O23' | 2.413 (3) | Cu—Cu' | 3.188 (3) |
| Cu'—O23' | 1.890 (2) | | |
| O23—Cu—O21 | 93.91 (9) | O23'—Cu'—N1' | 174.09 (8) |
| O23—Cu—N1 | 174.37 (9) | O21'—Cu'—N1' | 92.05 (9) |
| O21—Cu—N1 | 91.72 (10) | O23'—Cu'—N10' | 93.28 (9) |
| O23—Cu—N10 | 93.56 (9) | O21'—Cu'—N10' | 165.63 (9) |
| O21—Cu—N10 | 167.55 (9) | N1'—Cu'—N10' | 80.93 (9) |
| N1—Cu—N10 | 80.92 (10) | O23'—Cu'—O23 | 85.22 (9) |
| O23—Cu—O23' | 86.06 (9) | O21'—Cu'—O23 | 102.4 (1) |
| O21—Cu—O23' | 101.06 (9) | N1'—Cu'—O23 | 93.66 (9) |
| N1—Cu—O23' | 92.71 (9) | N10'—Cu'—O23 | 90.60 (9) |
| N10—Cu—O23' | 89.38 (9) | Cu—O23'—Cu' | 94.85 (9) |
| O23'—Cu'—O21' | 93.85 (9) | Cu—O23—Cu' | 93.83 (9) |

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

| D—H...A | D—H | H...A | D...A | D—H...A |
|------------------------------|----------|----------|-----------|---------|
| O52—H52...OW1 ⁱ | 0.87 (4) | 1.69 (4) | 2.541 (3) | 168 (3) |
| OW1—H1A...O22 | 0.95 | 1.81 | 2.737 (3) | 168 |
| OW1—H1B...O22 ⁱⁱ | 0.95 | 1.82 | 2.766 (3) | 174 |
| OW2—H2B...O22 ⁱⁱⁱ | 0.93 | 1.90 | 2.816 (3) | 169 |
| OW2—H2A...O22 ^{iv} | 0.95 | 2.20 | 3.140 (4) | 174 |

Symmetry codes: (i) $x, 1 + y, z$; (ii) $-x, -y, 1 - z$; (iii) $x, y, z - 1$; (iv) $-x, 1 - y, 1 - z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Nonius* (unpublished). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *CAMERON* (Watkin *et al.*, 1996). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1051). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 2070–2073

3-Hydroxyphthalide and its adduct with dibutyltin oxide

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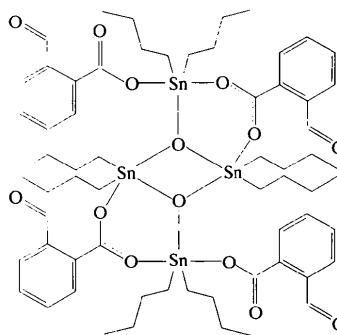
(Received 9 June 1999; accepted 31 August 1999)

Abstract

3-Hydroxyphthalide, C₈H₆O₃, reacts with dibutyltin oxide to give bis{μ₃-oxo-(μ-2-formylbenzoato-*O*:*O'*)-(2-formylbenzoato-*O*)bis[dibutyltin(IV)]}, [Sn₄(C₄H₉)₈-(C₈H₅O₃)₄(μ-*O*)₂], in which the four Sn atoms are all five-coordinated to three O and two C atoms arranged at the corners of a distorted trigonal bipyramid. The equatorial Sn—μ₃-O distances are in the range 2.039 (2)–2.048 (2) Å and are significantly shorter than the axial Sn—μ₃-O distances of 2.170 (3) and 2.182 (2) Å. The Sn—O_{carboxylate} bonds are all axial and have distances in the range 2.204 (3)–2.271 (3) Å, which are inversely correlated with the respective C—O bond distances. The mean Sn—C distance is 2.136 (6) Å. 3-Hydroxyphthalide undergoes ring opening to give the anion of 2-formylbenzoic acid which bonds to the Sn atoms. The structure of 3-hydroxyphthalide is stabilized by O—H...O hydrogen bonds [O...O = 2.766 (1) Å] which link the molecules in a zigzag chain parallel to *b*.

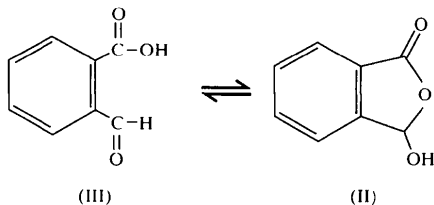
Comment

The reaction between *o*-substituted aromatic carboxylic acids with diorganotin oxide yields two types of diorganotin carboxylate, *i.e.* with a 2:1 or a 1:1 ligand–tin ratio (Gielen *et al.*, 1992, 1993). As a continuation of our studies of the structure–activity relationship (Goh *et al.*, 1998), we report the structures of the prod-



(I)

ucts of the reaction between 3-hydroxyphthalide, (II), and dibutyltin oxide. Whilst the 1:1 reaction mixture yielded dimeric bis{ μ_3 -oxo-(μ -2-formylbenzoato-*O*:*O'*)-(2-formylbenzoato-*O*)bis[dibutyltin(IV)]}, (I), the only crystalline product from the 2:1 mixture was 3-hydroxyphthalide. The crystal structures of (I) and (II) are reported here. The dimeric compound (Fig. 1) consists



of a roughly planar arrangement of an (Sn₂O)₂ core and 2-formylbenzoate groups, with the *n*-butyl groups above and below the plane, and pairs of Sn atoms being bridged by carboxylate groups. The Sn atoms are all five-coordinated with a distorted trigonal bipyramidal arrangement of three O and two C atoms. There are two types of Sn atoms: Sn1 and Sn3 are bonded to two carboxyl O and one μ_3 -O atom, whilst Sn2 and Sn4 are bonded to one carboxyl O and two μ_3 -O atoms.

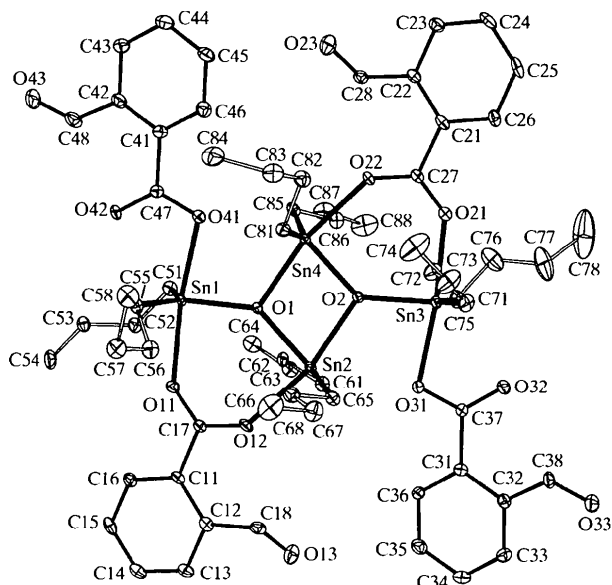


Fig. 1. View of (I). Displacement ellipsoids are shown at the 30% probability level.

The equatorial Sn— μ_3 -O distances are in the range 2.039 (2)–2.048 (2) Å, with a mean value of 2.044 (4) Å, and are significantly shorter than the axial Sn— μ_3 -O distances of 2.170 (3) and 2.182 (2) Å, as is expected (Clare & Kepert, 1994). The Sn—O_{carboxylate} bonds are all axial and have distances in the range 2.204 (3)–2.271 (3) Å, which are inversely correlated with the respective C—O bond distances [$d_{\text{SnO}} = 4.15(17)$ – $1.51(13)d_{\text{CO}}$]. The Sn—C distances vary be-

tween 2.130 (4) and 2.151 (4) Å, with a mean of 2.136 (6) Å.

There are close contacts of *ca* 2.8 Å between each Sn and a carboxyl O atom which cap a face defined by two C atoms and an apical O atom. These close contacts may account for the distortion of the bipyramids for which the C—Sn—C angles are 138.5 (1)–144.5 (2)° and the apical O atom is bent away from the capping O atom so that O_{ax}—Sn—O_{ax} angles are 166.3 (1)–173.5 (1)°.

2-Formylbenzoic acid, C₈H₆O₃, can exist in either of two tautomeric forms, *i.e.* as 3-hydroxyphthalide, (II), or as carboxybenzaldehyde, (III). IR (Bernatek, 1960) and NMR measurements (Kagen, 1967) showed that whilst it exists in solution as the cyclized form (II), treatment with alkali leads to ring opening and gives the anion of (III). We find that in the solid state the compound exists as the phthalide (Fig. 2), although it reacts with dibutyltin oxide as the open form (III). The 3-hydroxyphthalide molecule has the expected geometry and the molecules are linked by O—H...O hydrogen bonds in a zigzag chain along the *b* axis.

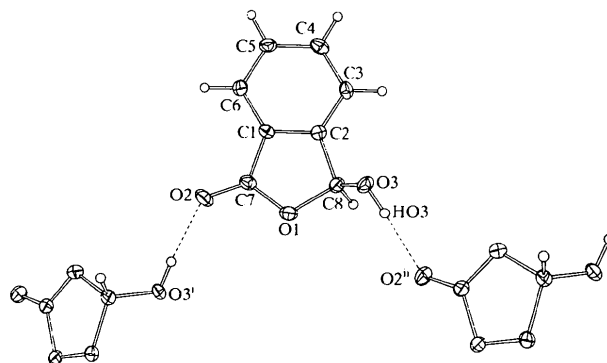


Fig. 2. View of (II) showing the labelling of the non-H atoms and the hydrogen bonding. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as small circles of an arbitrary radius. [Symmetry codes: (i) $-x, \frac{1}{2} + y, -z$; (ii) $-x, y - \frac{1}{2}, -z$.]

Experimental

Bis{ μ_3 -oxo-(μ -2-formylbenzoato-*O*:*O'*)-(2-formylbenzoato-*O*)bis[dibutyltin(IV)]}, (I), was synthesized by mixing equimolar amounts (10 mmol) of 3-hydroxyphthalide and dibutyltin oxide in dry benzene (50 ml). After refluxing with a Dean–Stark apparatus for 3–4 h, the reaction mixture was concentrated, cooled and triturated with petroleum ether (333–353 K) to yield a white solid (3.35 g, m.p. 399–401 K). The isolated solid was recrystallized from benzene–petroleum ether (2:10) to give crystals of the pure compound (m.p. 403–405 K) suitable for X-ray analysis. When the above reaction was repeated with a 2:1 ratio of 3-hydroxyphthalide (20 mmol) and dibutyltin oxide (10 mmol), a white solid (4.38 g, m.p. 335–343 K) was obtained. Recrystallization ($\times 2$) of the solid from benzene–petroleum ether (1:1) yielded colourless crystals (m.p. 367–369 K) which were shown by X-ray crystallography to be 3-hydroxyphthalide.

Compound (I)*Crystal data*[Sn₄(C₄H₉)₈(C₈H₅O₃)₄(O)₂] $M_r = 1560.14$

Triclinic

 $P\bar{1}$ $a = 12.1605 (6) \text{ \AA}$ $b = 12.4140 (6) \text{ \AA}$ $c = 25.061 (1) \text{ \AA}$ $\alpha = 83.771 (1)^\circ$ $\beta = 82.672 (1)^\circ$ $\gamma = 62.875 (1)^\circ$ $V = 3334.1 (2) \text{ \AA}^3$ $Z = 2$ $D_x = 1.554 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Siemens SMART CCD diffractometer

 ω rotation scans with narrow frames

Absorption correction: by integration (XPREP; Siemens, 1995)

 $T_{\min} = 0.611$, $T_{\max} = 0.775$

19 727 measured reflections

11 985 independent reflections

*Refinement*Refinement on F $R = 0.037$ $wR = 0.037$ $S = 1.24$

10 872 reflections

740 parameters

H atoms constrained

 $w = 1/\{\sigma_{cs}(F^2) + 1.03F^2\}^{1/2} - |F|\}^2$ $(\Delta/\sigma)_{\max} = 0.020$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8121 reflections

 $\theta = 1.6\text{--}27.7^\circ$ $\mu = 1.541 \text{ mm}^{-1}$ $T = 120 \text{ K}$

Block

 $0.42 \times 0.28 \times 0.18 \text{ mm}$

Colourless

10 872 reflections with $I > 3\sigma(I)$ $R_{\text{int}} = 0.049$ $\theta_{\max} = 25^\circ$ $h = -15 \rightarrow 15$ $k = -16 \rightarrow 15$ $l = -29 \rightarrow 31$

Intensity decay: none

 $\Delta\rho_{\max} = 1.4 (1) \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -1.3 (1) \text{ e \AA}^{-3}$

Extinction correction:

B—C type 1, Lorentzian isotropic (Becker & Coppens, 1974)

Extinction coefficient:

 $14 (2) \times 10^2$ Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Monoclinic

 $P2_1$ $a = 3.9463 (6) \text{ \AA}$ $b = 11.423 (2) \text{ \AA}$ $c = 7.3270 (11) \text{ \AA}$ $\beta = 97.020 (3)^\circ$ $V = 327.80 (9) \text{ \AA}^3$ $Z = 2$ $D_x = 1.521 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Siemens SMART CCD diffractometer

 ω rotation scans with narrow frames

Absorption correction: none

6310 measured reflections

1006 independent reflections

*Refinement*Refinement on F $R = 0.028$ $wR = 0.037$ $S = 1.70$

1004 reflections

103 parameters

H atoms treated by a mixture of independent and constrained refinement

Cell parameters from 4235 reflections

 $\theta = 2.8\text{--}34.1^\circ$ $\mu = 0.117 \text{ mm}^{-1}$ $T = 120 \text{ K}$

Plate

 $0.48 \times 0.44 \times 0.16 \text{ mm}$

Colourless

1004 reflections with $I > 0$ $R_{\text{int}} = 0.041$ $\theta_{\max} = 30^\circ$ $h = -5 \rightarrow 5$ $k = -14 \rightarrow 17$ $l = -11 \rightarrow 11$

Intensity decay: none

 $w = 1/\{\sigma_{cs}(F^2) + 1.03F^2\}^{1/2} - |F|\}^2$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.27 (4) \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.21 (4) \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Table 2. *Hydrogen-bonding geometry* (\AA , $^\circ$) for (II)

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------|----------|----------|-----------|---------|
| O3—HO3...O2' | 0.82 (3) | 1.96 (3) | 2.766 (1) | 173 (2) |

Symmetry code: (i) $-x, \frac{1}{2} + y, -z$.H atoms were placed in calculated positions (C—H = 0.95 \AA) with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the atom to which they were attached, except for the hydroxyl-H atom of 3-hydroxyphthalide which was refined isotropically.For both compounds, data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structures: SIR97 (Casarano *et al.*, 1996) in KRYSTAL (Hazell, 1995); program(s) used to refine structures: modified ORFLS (Busing *et al.*, 1962) in KRYSTAL; molecular graphics: ORTEPIII (Burnett & Johnson, 1996) in KRYSTAL; software used to prepare material for publication: KRYSTAL.

Financial support was received from the National Institute of Education, Singapore (RP18/96KLE) and from the Carlsberg Foundation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1568). Services for accessing these data are described at the back of the journal.

Table 1. *Selected bond lengths* (\AA) for (I)

| | | | |
|---------|-----------|---------|-----------|
| Sn1—O1 | 2.048 (3) | Sn3—C71 | 2.136 (4) |
| Sn1—O11 | 2.266 (3) | Sn3—C75 | 2.140 (4) |
| Sn1—O41 | 2.211 (3) | Sn4—O1 | 2.182 (3) |
| Sn1—C51 | 2.151 (4) | Sn4—O2 | 2.046 (3) |
| Sn1—C55 | 2.130 (4) | Sn4—O22 | 2.249 (3) |
| Sn2—O1 | 2.041 (3) | Sn4—C81 | 2.130 (4) |
| Sn2—O2 | 2.170 (3) | Sn4—C85 | 2.134 (4) |
| Sn2—O12 | 2.248 (3) | O11—C17 | 1.251 (5) |
| Sn2—C61 | 2.132 (4) | O12—C17 | 1.267 (5) |
| Sn2—C65 | 2.136 (4) | O21—C27 | 1.245 (5) |
| Sn3—O2 | 2.039 (3) | O22—C27 | 1.265 (5) |
| Sn3—O21 | 2.271 (3) | O31—C37 | 1.288 (5) |
| Sn3—O31 | 2.204 (3) | O41—C47 | 1.289 (5) |

Compound (II)*Crystal data*C₈H₆O₃ $M_r = 150.14$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ **References**Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
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Acta Cryst. (1999). **C55**, 2073–2075

**Poly[[tetraaquapraesodymium(III)- μ -
(iminodiacetato- $O,O':O':O'',O''':O''')$]
dichloride hydrate]**

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(Received 6 April 1999; accepted 9 September 1999)

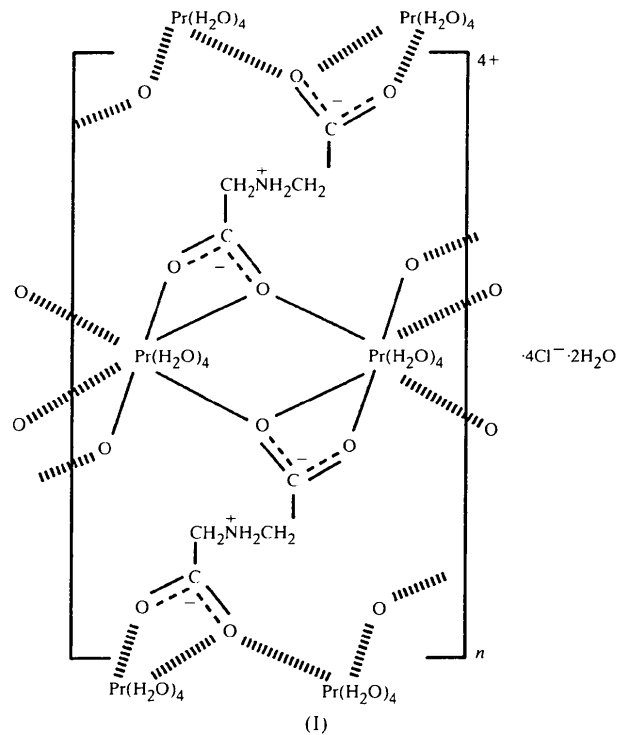
Abstract

The title compound, $[\text{Pr}(\text{C}_4\text{H}_6\text{NO}_4)(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$, consists of $[\text{Pr}(\text{OOCCH}_2\text{NH}_2\text{CH}_2\text{COO})(\text{H}_2\text{O})_4]$ sheets, Cl^- ions and solvent water molecules. Within the sheets, each Pr ion is linked by four bridging iminodiacetate ligands and is further coordinated by four water molecules giving a distorted bicapped square antiprism coordination environment with an average Pr—O distance of 2.573(2) Å. The Cl^- ions and the solvent water molecules lie between these sheets and form numerous hydrogen bonds with the coordinated water and the $-\text{NH}_2^-$ group of the ligand.

Comment

Amino acids and polyamino acids are widely used to form rare earth complexes (Huang, 1997). Among them

those with iminodiacetic acid were studied extensively about 30 years ago, but the available crystal structures are quite limited (Albertsson & Oskarsson, 1968, 1974; Li *et al.*, 1997; Oskarsson, 1971). This might be due to the fact that crystal structures in this series are often isostructural, as well as the often poor quality of crystals obtained (Albertsson & Oskarsson, 1974; Oskarsson, 1971). Recently, we synthesized the title compound, (I), and obtained crystals of high quality. Its structure belongs to a new type, which is reported here.



Each praesodymium(III) ion in (I) is coordinated by four carboxylate groups from four iminodiacetate ligands and each ligand links four different praesodymium ions (Fig. 1). All the carboxylate groups have a bidentate and a bridging-type mode (Dong *et al.*, 1990; Imai *et al.*, 1987). For each carboxylate group, the two O atoms coordinate to one Pr^{3+} ion and one of them, the μ -O, coordinates to another Pr^{3+} ion. Along the c direction, Pr^{3+} ions are connected by the μ -O atoms (O2 and O3) to form chains, which are connected by the ligands to build up a two-dimensional network parallel to the ac plane. This connection mode is quite different from the structures of all other known complexes of rare earth ions with iminodiacetic acid (Albertsson & Oskarsson, 1968, 1974; Li *et al.*, 1997; Oskarsson, 1971).

The coordination environment around the Pr^{3+} ion is a distorted bicapped square antiprism made up of six O atoms from four carboxylate groups and four coordinated water molecules, *i.e.* the Pr^{3+} ion is decacoordinated [coordination number (CN) = 10]. The μ -O atoms give one long and one short Pr—