Synthesis and Structural Characterization of Tin(II) and Zinc(II) Derivatives of Cyclic α-Hydroxyketones, Including the Structures of Sn(maltol)₂, Sn(tropolone)₂, Zn(tropolone)₂, and Zn(hinokitiol)₂

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Zinc(II) and tin(II) derivatives of maltol (Hmalt), ethylmaltol (HEtmalt), tropolone (Htrop), hinokitiol (Hhino), and kojic acid (Hkoj) have been prepared and characterized, and the crystal structures of M(trop)₂ (M = Zn, Sn), Zn(hino)₂·EtOH, and Sn(malt)₂ have been determined. The Zn(trop)₂ is a polymeric structure in which tropolone has both a bridging and chelating role; zinc(hino)₂ crystallizes as an ethanol adduct of which the structure is a dimeric fragment of the Zn(trop)₂ polymer and in which each metal is "capped" by a molecule of alcohol. The tin complexes are notably air-stable despite adopting monomeric pseudo-trigonal-bipyramidal structures (SnO₄E; E is a stereochemically active lone electron pair) in which the ligands only chelate a single metal center.

Introduction

Zinc has been widely used in dental care formulations for many years, usually in the form of zinc(II) citrate.[1] Similarly, SnF₂ has been incorporated into toothpaste for over 2 decades[2] primarily as a convenient fluoride source but more recently the inherent antimicrobial activity of the tin itself has also been appreciated.[3−5] We are actively engaged in a program of work which involves the design and synthesis of orally viable derivatives of these two metals which may show enhanced biological activity. In particular for tin, there is a need to deliver the metal in an accessible form while stabilizing the lower oxidation state. Issues such as solubility need to be balanced against the inherent oxidative instability of the stannous ion. Thus, complexes in which a ligand set crowds the tin lone pair need to involve minimal intermolecular metal−ligand interactions which inhibit solubility. While oxidation state stability is not an issue for Zn(II), the choice of ligand for both metals is further restricted by its own inherent oral acceptability.

We have found that cyclic α-hydroxyketones as a generic class contain species such as maltol (**Ia**; Hmalt), ethylmaltol (**Ib**; HEtmalt), and hinokitiol (**IIb**; Hhino) which fulfill many of the above requirements.
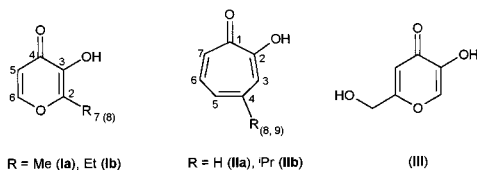
R = Me (Ia), Et (Ib)　　　R = H (IIa), iPr (IIb)　　　(III)

Maltol and ethylmaltol are approved food additives, while hinokitiol is known to exhibit biological activity in its own right.[6] All three are capable of chelating, and hence stabilizing, metal centers. We have recently reported the efficacy of M(II) derivatives (M = Zn, Cu, Sn) of these ligands in oral care formulations,[7] along with a more fundamental study of the structures of various X₂SnL₂ species [X = F, Cl; L = malt, Etmalt, hino].[8] We now report on the synthesis and structural characterization of M(II) compounds containing these three ligands, along with derivatives of the related ligands tropolone (**IIa**; Htrop) and kojic acid (**III**; Hkoj). Kojic acid has previously been used in cosmetics as a whitening agent because of its ability to inhibit tyrosinase, which is responsible for melanization in animals and browning in plants.[9]

Experimental Section

General Methods. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Nicolet 510P FT-IR spectrophotometer; elemental analyses were performed using a Carlo-Erba Strumentazione E.A. model 1106 microanalyzer operating at 500 °C. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-GX270 FT spectrometer, while ¹¹⁹Sn NMR spectra were recorded on a JEOL JNM-EX400 FT machine, all using saturated CDCl₃ solutions unless indicated otherwise. Details of our Mössbauer spectrometer and related procedures are given elsewhere.[10] Mössbauer spectra were recorded on solid samples at 77 K. Starting materials were commercially obtained and used without

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[†] University of Bath.
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(1) Hoeven, J. S. v. d.; Cummins, D.; Schaeken, M. J. M.; Ouderaa, F. J. G. v. d. *Caries Res.* **1993**, *27*, 298.
(2) Tinanoff, N. *J. Clin. Dent.* **1990**, *6*, 37.
(3) Addy, M. *J. Clin. Periodontol.* **1986**, *13*, 957.
(4) Beiswanger, B. B.; Doyle, P. M.; Jackson, R. D.; Mallatt, M. E.; Mau, M. S.; Bollmer, B. W.; Crisanti, M. M.; Guay, C. B.; Lanzalaco, A. C.; Lucacovic, M. F.; Majeti, S.; McClanaghan, L. K. *J. Clin. Dent.* **1995**, *6*, 46.
(5) Perlich, M. A.; Bacca, L. A.; Bollmer, B. W.; Lanzalco, A. C.; McClanaghan, L. K.; Sewak, L. K.; Beiswanger, B. B.; Eichold, W. A.; Hull, J. R.; Jackson, R. D.; Mau, M. S. *J. Clin. Dent.* **1995**, *6*, 54.
(6) Erdtmann, H.; Gripenberg, J. *Nature* **1948**, *161*, 719.
(7) Creeth, J.; Molloy, K. C.; Wright, P. Oral Cove Compositions. International Patent WO 00/16736, 2000.
(8) Barret, M. C.; Mahon, M. F.; Molloy, K. C.; Wright, P. *Main Group Met. Chem.* **2000**, *23*, 663.
(9) Cabanes, J.; Chazarra, S.; Garcia-Carmona, F. *J. Pharm. Pharmacol.* **1994**, *46*, 982.
(10) Molloy, K. C.; Purcell, T. G.; Quill, K.; Nowell, I. *J. Organomet. Chem.* **1984**, *267*, 237.

further purification. Tin(II) *n*-butoxide was freshly made by suspending Sn(OMe)$_2$ in dry toluene and adding sufficient *n*-butanol to bring about dissolution.[11] The resulting clear solution was used immediately.

Syntheses. Zn(malt)$_2$·2H$_2$O (1). A solution of maltol (1.27 g, 10.00 mmol) in water/ethanol mix (25 mL/25 mL) was added to a well-stirred solution of zinc acetate (1.09 g, 4.96 mmol) in the same solvent mixture. After stirring for 2 h, the solution was refluxed and stirred for another 2 h and then left at room temperature. A pale yellow crystalline product appeared (0.79 g, 45%). Analysis, found [calcd for C$_{12}$H$_{14}$O$_8$Zn]: C 39.8 (40.9), H 4.19 (4.02). ^{1}H NMR [δ (ppm)]: 2.34 [3H, s, CH_3]; 6.54 [1H, d, H_6; J = 5.1 Hz]; 8.12 [1H, d, H_5]. ^{13}C NMR [δ (ppm)]: 14.8 [C_7]; 109.8 [C_5]; 149.8 [C_6]; 151.7 [C_3]; 153.6 [C_2]; 177.6 [C_4]. IR data (cm^{-1}): 3500 broad ν(H−O−H), 1614, 1578 ν(C=O); 1517 ν(C=C); 1277, 1202 ν(C−O).

Zn(Etmalt)$_2$·2H$_2$O (2). By the use of the same procedure using ethylmaltol (2.00 g, 14.28 mmol) in water/ethanol mix (25 mL/25 mL) and zinc acetate (1.57 g, 7.15 mmol) in water/ethanol mix (25 mL/25 mL), **2** was obtained as a beige solid (0.79 g, 45%). Analysis, found [calcd for C$_{14}$H$_{18}$O$_8$Zn]: C 44.5 (44.3), H 4.83 (4.79). ^{1}H NMR [δ (ppm)]: 1.16 [3H, t, CH_3; J = 7.5 Hz]; 2.79 [2H, q, CH_2; J = 7.5 Hz]; 6.55 [1H, d, H_6; J = 5.2 Hz]; 8.16 [1H, d, H_5; J = 5.2 Hz]. ^{13}C NMR [δ (ppm)]: 11.4 [C_8]; 21.4 [C_7]; 109.7 [C_5]; 151.0 [C_6]; 153.7 [C_3]; 154.1 [C_2]; 177.9 [C_4]. IR data (cm^{-1}): 3480 broad ν(H−O−H), 1595, 1570 ν(C=O); 1508 ν(C=C); 1280, 1193 ν(C−O).

Zn(trop)$_2$ (3). The method described previously for **2** was repeated using tropolone (0.50 g, 4.09 mmol) in water/ethanol mix (5 mL/5 mL) added to zinc acetate (0.45 g, 2.05 mmol) in the same solvent system (50 mL). Following this procedure, yellow crystals suitable for X-ray crystallography were obtained (0.56 g, 89%). Analysis, found [calcd for C$_{14}$H$_{10}$O$_4$Zn]: C 54.2 (54.8), H 3.33 (3.26). IR data (cm^{-1}): 1620, 1582 ν(C=O); 1523 ν(C=C); 1265, 1213 ν(C−O).

Zn(hino)$_2$ (4). Hinokitiol (0.20 g, 1.22 mmol) was dissolved in aqueous ethanol (1:1, 50 mL) with stirring. To this, a solution of zinc-(II) acetate (0.13 g, 0.61 mmol) in the same solvent was added, and the mixture was refluxed gently for 2 h. After 1 week, a solid had precipitated which was recrystallized from toluene to yield **4** (0.08 g, 33%). Analysis, found [calcd for C$_{20}$H$_{22}$O$_4$Zn]: C 61.3 (60.9), H 5.67 (5.63). ^{1}H NMR [δ (ppm), d^6-DMSO]: 7.36 (dd, 1H, H_4; J = 11.0, 10.1 Hz), 7.18 (s, 1H, H_7), 7.07 (d, 1H, H_5; J = 11.0 Hz), 6.86 (d, 1H, H_3; J = 10.1 Hz), 2.85 (m, 1H, H_8), 1.21 (d, 6H, CH_3; J = 6.8 Hz). ^{13}C NMR [δ (ppm), d^6-DMSO]: 23.7 [C_9]; 39.1[C_8]; 122.3, 123.4, 123.6 [$C_{4,5,7}$]; 137.3 [C_3]; 159.1 [C_6]; 177.7, 178.2 [$C_{1,2}$]. IR data (cm^{-1}): 1597, 1576 ν(C=O); 1504 ν(C=C).

Recrystallization from ethanol/hexane (1:1) yields the 1:1 ethanol solvate (**4a**) as yellow crystals. Analysis, found [calcd for C$_{22}$H$_{28}$O$_5$-Zn]: C 60.4 (60.6), H 6.46 (6.19).

Sn(malt)$_2$ (5). A solution of maltol (10.46 g, 83.0 mmol) in dry toluene (100 mL) was added to a well-stirred solution of (^{n}BuO)$_2$Sn[11] (10.98 g, 41.5 mmol) in dry toluene (200 mL) under nitrogen. The solution was stirred for 2 h. The solution was left at room temperature and, on standing, yielded pale yellow crystals suitable for X-ray crystallography (6.02 g, 39%). Analysis, found [calcd for C$_{12}$H$_{10}$O$_6$-Sn]: C 39.0 (39.0), H 2.75 (2.71). ^{1}H NMR [δ (ppm)]: 2.39 [3H, s, CH_3]; 6.83 [1H, d, H_6; J = 5.13 Hz]; 8.35 [1H, d, H_5; J = 5.13 Hz]. ^{13}C NMR [δ (ppm)]: 15.5 [C_7]; 111.8 [C_5]; 148.2 [C_2]; 153.8 [C_3]; 155.6 [C_6]; 177.7 [C_4]. IR data (cm^{-1}): 1570 ν(C=O); 1504 ν(C=C); 1265, 1199 ν(C−O). Mössbauer data (mm s^{-1}): IS = 2.96, QS = 1.99.

Sn(Etmalt)$_2$ (6). The method described previously for **5** was followed using ethylmaltol (14.00 g, 100.0 mmol) in dry toluene (50 mL) and (^{n}BuO)$_2$Sn (13.23 g, 50.0 mmol) in dry toluene (200 mL). This yielded **6** as a pale yellow solid (13.06 g, 66%). Analysis, found [calcd for C$_{14}$H$_{14}$O$_6$Sn]: C 42.4 (42.3), H 3.61 (3.53). ^{1}H NMR [δ (ppm)]: 1.08 [3H, t, CH_3]; 2.75 [2H, q, CH_2]; [1H, d, H_6; J = 5.27 Hz]; 7.76 [1H, d, H_5; J = 4.98 s Hz]. ^{13}C NMR [δ (ppm)]: 11.2 [C_8]; 22.4 [C_7]; 111.9 [C_5]; 153.0 [C_2]; 154.9 [C_6]; 158.8 [C_3]; 178.1 [C_4]. IR data (cm^{-1}): 1564 ν(C=O); 1509 ν(C=C); 1261, 1191 ν(C−O). Mössbauer data (mm s^{-1}): IS = 3.01, QS = 2.01.

Sn(trop)$_2$ (7). The method described previously for **5** was repeated using tropolone (1.00 g, 8.2 mmol) in dry toluene (20 mL) and (^{n}-

(^{n}BuO)$_2$Sn (1.08 g, 4.1 mmol) in dry toluene (80 mL). This yielded **7** as a pale yellow solid (0.55 g, 37%). Analysis, found [calcd for C$_{14}$H$_{10}$O$_4$-Sn]: C 46.6 (46.6), H 3.00 (2.77). ^{1}H NMR [δ (ppm)]: 7.14−7.64 (m, 5H, C$_7H_5$). ^{13}C NMR [δ (ppm)]: 124.3 [C_3]; 126.8 [C_4]; 139.7 [C_2]; 178.6 [C_1]. IR data (cm^{-1}): 1593 ν(C=O); 1509 ν(C=C); 1254 ν(C−O). Mössbauer data (mm s^{-1}): IS = 2.91, QS = 1.98.

Sn(hino)$_2$ (8). Hinokitiol (0.50 g, 3.04 mmol) in ethanol (10 mL) was added to a well-stirred solution of tin(II) chloride dihydrate (0.34 g, 1.52 mmol) in water (20 mL) under nitrogen. The water was previously degassed for 1 h. A precipitate appeared after 30 min, and the solution was stirred for another hour. The solution was cannula filtered, and **8** was dried under in vacuo (0.38 g, 56%). Analysis, found [calcd for C$_{20}$H$_{22}$O$_4$Sn]: C 54.2 (53.9), H 5.01 (4.95). ^{1}H NMR [δ (ppm)]: 1.21 [6H, d, CH_3]; 2.83 [1H, sept, H_8]; 6.95 [1H, s, H_7]; 7.26−7.43 [3H, m, H_3, H_4, H_5]. ^{13}C NMR [δ (ppm)]: 23.7 [C_9]; 39.1 [C_8]; 125.2 [C_7]; 126.4 [C_3]; 127.1 [C_5]; 138.0 [C_4]; 160.8 [C_6]; 177.0 [C_2]; 177.5 [C_1]. IR data (cm^{-1}): 1601 ν(C=O); 1524 ν(C=C); 1240, 1179 ν(C−O). Mössbauer data (mm s^{-1}): IS = 2.84, QS = 1.92.

Zn(koj)$_2$ (9). The methodology described for **1** was employed using kojic acid (0.50 g, 3.52 mmol) in water/ethanol mix (5 mL/5 mL) and zinc acetate (0.39 g, 1.76 mmol) in the same solvent mixture (50 mL). Compound **9** precipitated from solution as a white solid (0.50 g, 82%) which was insoluble in common organic solvents. Analysis, found [calcd for C$_{12}$H$_{10}$O$_6$Zn]: C 41.2 (41.4), H 3.05 (2.88). IR data (cm^{-1}): 3500 broad ν(O−H), 1614, 1578 ν(C=O); 1517 ν(C=C); 1277, 1202 ν(C−O).

Sn(koj)$_2$ (10). The methodology described for **5** was employed with kojic acid (0.82 g, 5.79 mmol) in dry toluene (60 mL) and (^{n}BuO)$_2$Sn (0.76 g, 2.88 mmol) in dry toluene (80 mL). Compound **10** precipitated from solution as a yellow solid (0.52 g, 45%) which was insoluble in common organic solvents. Analysis, found [calcd for C$_{12}$H$_{10}$O$_6$Sn]: C 37.9 (41.7), H 2.85 (2.77). IR data (cm^{-1}): 3269 ν(O−H); 1572 ν(C=O); 1521 ν(C=C); 1261, 1147 ν(C−O). Mössbauer data (mm s^{-1}): IS = 3.11, QS = 1.95.

X-ray Crystallography. Experimental and crystal data for **3**, **4a**, **5**, and **7** are given in Table 1; the asymmetric units are shown in Figures 1−4 and the figures include selected metrical data. Data for **3** were collected on an Enraf-Nonius CAD-4 diffractometer, while data for **4a**, **5**, and **7** were collected on a Nonius Kappa CCD machine. Data for the latter two compounds were collected on crystals with a very thin platelike appearance, and poor crystal quality is responsible for the high R-factor for **7**. For all four compounds, data were corrected for both extinction and absorption effects; hydrogens were added at calculated positions. Refinement was full matrix least-squares based on F^2. Structure determination and refinement were achieved using the SHELX suite of programs;[12,13] drawings were produced using ORTEX.[14]

Results and Discussion

Synthesis and Spectroscopy. Zinc(II) derivatives of the cyclic α-hydroxyketones maltol, ethylmaltol, tropolone, and hinokitiol can be straightforwardly prepared from the reaction of zinc(II) acetate and ligand (1:2) in a water/ethanol mixture. The products (**1**−**4**) crystallize on standing:
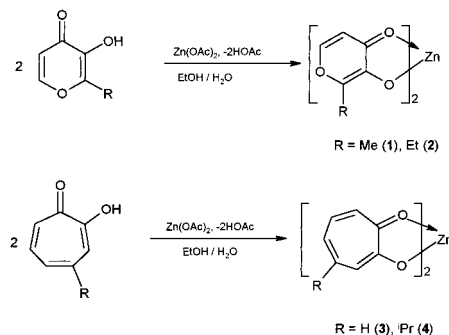
R = Me (1), Et (2)

R = H (3), ^{i}Pr (4)

(11) Gsell, R.; Zeldin, M. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1133.

Both **1** and **2** crystallize as dihydrates, while **3** and **4** are both

Table 1. Crystal Data Structure Refinement Details for Compounds **3**, **4a**, **5**, and **7**[a]

|	**3**	**4a**	**5**	**7**
empirical formula	$C_{14}H_{10}O_4Zn$	$C_{22}H_{28}O_5Zn$	$C_{12}H_{10}O_6Sn$	$C_{14}H_{10}O_4Sn$
fw	307.59	437.81	368.89	360.91
temp, K	293(2)	170(2)	100(2)	120(2)
cryst syst	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P2_1/n$	$Fdd2$	$P\bar{1}$
unit cell dimensions				
a (Å), α (deg)	6.3438(6)	8.0820(2)	18.908(8)	7.4934(7), 78.140(6)
b (Å), β (deg)	20.504(2), 98.84(1)	17.1500(3),100.219(1)	26.355(8)	7.503(1), 84.493(6)
c (Å), γ (deg)	9.391(1)	14.9090(3)	4.971(2)	12.026(2), 74.096(5)
vol (Å³)	1207.0(2)	2033.70(7)	2477(2)	635.8(2)
Z	4	4	8	2
abs coeff (mm⁻¹)	2.040	1.238	2.083	2.016
cryst size (mm)	0.20 × 0.20 × 0.20	0.20 × 0.17 × 0.12	0.40 × 0.08 × 0.08	0.80 × 0.80 × 0.10
reflns collected	2449	27227	594	3801
independent reflns	2126 [R(int) = 0.0110]	4666 [R(int) = 0.0431]	440 [R(int) = 0.0525]	2192 [R(int) = 0.0989]
data/restraints/params	2123/0/173	4666/1/262	439/1/89	2192/0/173
final R indices [$I > 2\sigma(I)$] R1, wR2	0.0308, 0.0791	0.0288, 0.0734	0.0434, 0.1059	0.0987, 0.2524
R indices (all data) R1, wR2	0.0407, 0.0843	0.0375, 0.0774	0.0530, 0.1529	0.1044, 0.2550

[a] Additional crystallographic details are given in the Supporting Information.

anhydrous. Compound **4**, however, crystallizes from ethanol as a 1:1 solvate (**4a**). The hydrated nature of **1** has been noted by others.[15]

Initial attempts to prepare the analogous tin compounds from SnX_2 (X = Cl, F) resulted in formation of Sn(IV) species X_2-SnL_2 (L = malt, Etmalt, hino).[8] The desired compounds could, however, be readily prepared from $Sn(OBu^n)_2$[11] or $(C_5H_5)_2Sn$,[16] though in general the former proved more convenient as it could be generated in situ from $Sn(OMe)_2$, which in turn has good long-term stability when stored under N_2. In a typical experiment, $Sn(OMe)_2$ was suspended in toluene and excess ^nBuOH was added to bring about the formation of soluble $Sn(OBu^n)_2$. Two equivalents of the appropriate ligand was added, and the resultant solution yielded **5**–**8** on cooling over a period of days.
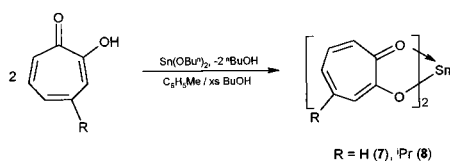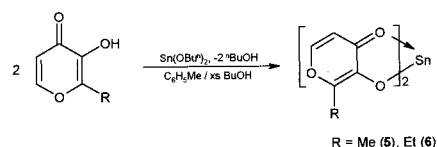

When the above methodologies were applied to the formation of tin(II) and zinc(II) derivatives of kojic acid, the products precipitated immediately from solution and proved to be insoluble in common organic solvents. This rendered both products difficult to purify and characterize, though the zinc complex (**9**) was analytically pure as isolated.
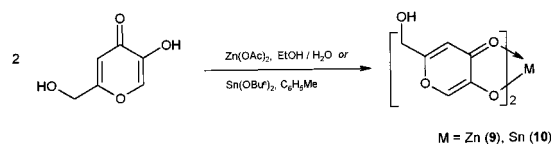
Presumably, the lowering of the solubility over **1**–**8** arises because the CH_2OH group involves itself in either intermolecular $CH_2(H)O:{\rightarrow}M$ coordination and/or extensive hydrogen bonding.

The long-term stability of the tin complexes is noteworthy. Stable Sn(II) species are not uncommon but are often associated with species where strong intermolecular interactions are present, e.g., oxides, halides, phosphates, etc. Monomeric derivatives are commonly less stable, such as the related $Sn(\beta\text{-diketonates})_2$ which are readily degraded in moist air to tin oxides. In contrast, the Mössbauer spectrum of **5** shows significantly less than 5% SnO_2 after 2 years of contact with air, though in chloroform solution open to the air, the compound is nearly completely decomposed to tin(IV) oxide in a week. The stability of the compound is of significance because (i) only the lower oxidation state is associated with antibacterial activity and (ii) toothpaste formulations routinely require long shelf lives during which the active ingredients are in contact with an aqueous, aerobic cocktail of other additives.

The aqueous stability of these tin compounds allows them to also be prepared in water, as exemplified by the synthesis of **8**:
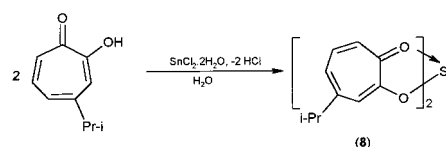
This is the preferred synthetic route for this compound as it is only sparingly soluble in common solvents and is difficult to separate from traces of oxide which can accrue from the use of the tin(II) alkoxide as starting material.

NMR spectra of **1**–**10** are unexceptional but confirm the stoichiometry of the products. Compounds **5**–**8** and **10** have Mössbauer isomer shift (is) values in the range of 2.91–3.11 mm s⁻¹ which clearly indicates tin in its divalent state, while the corresponding quadrupole splittings (qs, 1.95–2.01 mm s⁻¹) are all consistent with the presence of a stereochemically active lone electron pair. The systematic correlation of Mössbauer parameters and structure is, however, difficult for Sn(II) species as the metal coordination sphere is often distorted. For example,

(12) Sheldrick, G. M. *SHELX97L: A Program for Crystal Structure Determination*; University of Göttingen, Göttingen, Germany, 1986.

(13) Sheldrick, G. M. *SHELX97L: A Computer Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1997.

(14) McArdle, P. *J. Appl. Crystallogr.* **1995**, *28*, 65.

(15) Ahmed, S. I.; Burgess, J.; Fawcett, J.; Parsons, S. A.; Russell, D. R.; Laurie, S. H. *Polyhedron* **2000**, *19*, 129.

(16) Fischer, E. O.; Grubert, H. *Z. Naturforsch., B* **1956**, *11*, 423.
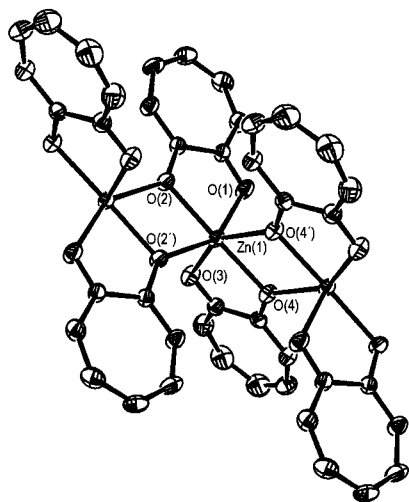
Figure 1. The structure of **3** highlighting the asymmetric unit and the labeling scheme used. Thermal ellipsoids are at the 30% probability level. Selected metrical data are as follows: Zn(1)−O(1), 2.067(2) Å; Zn(1)−O(2), 2.150(2) Å; Zn(1)−O(3), 2.051(2) Å; Zn(1)−O(4), 2.149-(2) Å; Zn(1)−O(2′), 2.121(2) Å; Zn(1)−O(4′), 2.103(2) Å; O(1)−C(1), 1.261(3) Å; O(2)−C(2), 1.291(3) Å; O(3)−C(8), 1.263(3) Å; O(4)−C(9), 1.299(3) Å; O(1)−Zn(1)−O(2), 74.84(7)°; O(1)−Zn(1)−O(3), 92.61(8)°; O(1)−Zn(1)−O(4), 103.19(7)°; O(1)−Zn(1)−O(2′), 146.82-(7)°; O(1)−Zn(1)−O(4′), 95.61(8)°; O(2)−Zn(1)−O(3), 101.47(7)°; O(2)−Zn(1)−O(4), 176.22(7)°; O(2)−Zn(1)−O(2′), 71.99(8)°; O(2)−Zn(1)−O(4′), 110.72(7)°; O(3)−Zn(1)−O(4), 75.29(7)°; O(3)−Zn(1)−O(2′), 93.21(8)°; O(3)−Zn(1)−O(4′), 147.81(7)°; O(4)−Zn(1)−O(2′), 109.89(7)°; O(4)−Zn(1)−O(4′), 72.54(7)°; O(2′)−Zn(1)−O(4′), 96.63-(7)°; Zn(1)−O(2)−Zn(1′), 108.01(8)°; Zn(1)−O(4)−Zn(1′), 107.46-(7)°.

the corresponding data for Sn(oxalate), which shows a similar stereochemistry of ligands about the metal, are IS = 3.47–3.70 mm s^{-1}, QS = 1.54–1.59 mm s^{-1}.[17,18] Infrared spectra of all the complexes reveal a shift in ν(C=O) by ca. 30–70 cm^{-1} from its position of ca. 1650 cm^{-1} in the corresponding free ligand, a phenomenon which has previously been noted in other metal complexes of these chelating ligands, e.g., Al(malt)$_3$.[19]

X-ray Crystallography. The structure of Zn(trop)$_2$ (**3**) is shown in Figure 1. Each tropolone ligand chelates zinc with a bite angle of 74.84(7)° [O(1)−Zn−O(2)] or 75.29(7)° [O(3)−Zn−O(4)] and, in addition, bridges, through only one of the available oxygen centers, to an adjacent metal. The result is a coordination polymer in which Zn$_2$O$_2$ rhomboids are linked in an orthogonally alternating manner. The coordination sphere about each zinc is that of a very distorted octahedron. In addition to the two bite angles which are dictated by the ligand to be less than 90°, the ∠O−Zn−O within each Zn$_2$O$_2$ rhombus are also less than 90° [∠O(2)−Zn−O(2′), 71.99(8)°; ∠O(4)−Zn−O(4′), 72.54(7)°]. The nominally trans pairs of atoms are thus generally at angles much reduced from 180° [∠O(1)−Zn−O(2′), 146.82(7)°; ∠O(3)−Zn−O(4′), 147.81(7)°] with only one such pair approximating to the ideal geometry [∠O(2)−Zn−O(4), 176.22(7)°]. Within each ligand, a short C=O [C(1)−O(1), 1.261(3) Å; C(8)−O(3), 1.263(3) Å] and a long C−O distance [C(2)−O(2), 1.291(3) Å; C(9)−O(4), 1.299(3) Å] can be identified, and surprisingly, it is the carbonyl oxygen which makes the shorter bond to zinc [Zn−O(1), 2.067(2) Å; Zn−
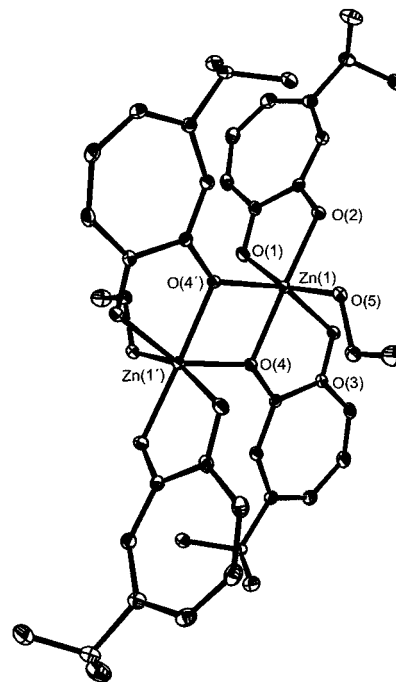

Figure 2. The structure of **4a** highlighting the asymmetric unit and the labeling scheme used. Thermal ellipsoids are at the 30% probability level. Selected metrical data are as follows: Zn(1)−O(1), 2.704(1) Å; Zn(1)−O(2), 2.029(1) Å; Zn(1)−O(3), 2.107(1) Å; Zn(1)−O(4), 2.075-(1) Å; Zn(1)−O(5), 2.258(1) Å; Zn(1)−O(4′), 2.171(1) Å; O(1)−C(1), 1.277(2) Å; O(2)−C(2), 1.287(2) Å; O(3)−C(12), 1.279(2) Å; O(4)−C(11), 1.306(2) Å; O(1)−Zn(1)−O(2), 78.63(5)°; O(1)−Zn(1)−O(3), 98.75(5)°; O(1)−Zn(1)−O(4), 99.39(5)°; O(1)−Zn(1)−O(5), 160.74-(4)°; O(1)−Zn(1)−O(4′), 90.68(5)°; O(2)−Zn(1)−O(3), 100.02(5)°; O(2)−Zn(1)−O(4), 175.63(5)°; O(2)−Zn(1)−O(5), 82.79(5)°; O(2)−Zn(1)−O(4′), 110.26(5)°; O(3)−Zn(1)−O(4), 76.35(4)°; O(3)−Zn(1)−O(5), 89.38(5)°; O(3)−Zn(1)−O(4′), 149.53(4)°; O(4)−Zn(1)−O(5), 99.48(4)°; O(4)−Zn(1)−O(4′), 73.54(5)°; O(5)−Zn(1)−O(4′), 91.03-(4)°; Zn(1)−O(4)−Zn(1′), 106.46(5)°. Symmetry operation is 1 − x, −y, −z.

O(3), 2.051(2) Å]. In uncomplexed tropolone itself, the C=O and C−O lengths are 1.261(3) and 1.333(3) Å, respectively.[20] The deprotonated oxygen of each ligand in **3** makes a weaker bond to zinc [Zn−O(2), 2.150(2) Å; Zn−O(4), 2.149(2) Å] presumably as a consequence of its ancillary bridging role [Zn−O(2′), 2.121 Å; Zn−O(4′), 2.103(2) Å]. On the basis of these bond length data, it appears that each tropolone bridges two zinc centers intermolecularly, supplemented by a weaker, intramolecular chelating role. The structure is related to the hydrated dimer [Ni(trop)$_2$(H$_2$O)]$_2$ in which one tropolone is chelating and the other bridging,[21] but in this latter case, waters of hydration effectively break the extended polymer seen in Zn-(trop)$_2$ to form "capped" dimers. In contrast, Cu(trop)$_2$ adopts a four-coordinate, square planar structure.[22]

The structure of the ethanol adduct of zinc(II) hinokitiol (**4a**) closely resembles that of **3,** and the former can be viewed as an ethanol-capped, dimeric fragment of the polymer adopted by **3** (Figure 2). The two hinokitiol ligands of **4a** orthogonally chelate the zinc, while one also has a bridging role. However, unlike **3**, one hinokitiol ligand in **4a** is purely chelating, with the remaining site in the zinc coodination sphere occupied by a weakly bound ethanol [Zn−O(5), 2.258(1) Å]. The bite angle

(17) Debye, N. W. G.; Fenton, D. E.; Zuckerman, J. J. *J. Inorg. Nucl. Chem.* **1972,** *34*, 352.
(18) Arifin, Z.; Filmore, E. J.; Donaldson, J. D.; Grimes, S. M. *J. Chem. Soc., Dalton Trans.* **1984,** 1965.
(19) Finnegan, M. M.; Rettig, S. J.; Orvig, C. *J. Am. Chem. Soc.* **1986,** *108*, 5033.

(20) Shimanouchi, H.; Sasada, Y. *Acta Crystallogr.* **1973,** *B29*, 81.
(21) Irving, R. J.; Post, M. L.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1973,** 697.
(22) Berg, J.-E.; Pilotti, A.-M.; Söderholm, A.-C.; Karlsson, B. *Acta Crystallogr.* **1978,** *B34*, 3071.
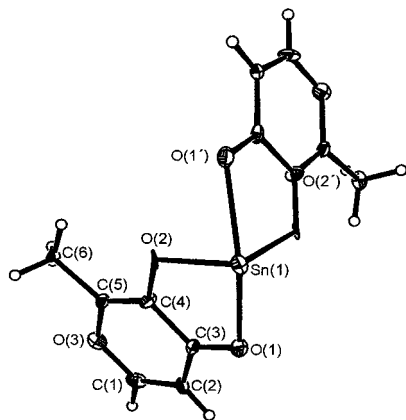
Figure 3. The structure of **5** highlighting the asymmetric unit and the labeling scheme used. Thermal ellipsoids are at the 30% probability level. Selected metrical data are as follows: Sn(1)−O(1), 2.324(8) Å; Sn(1)−O(2), 2.129(8) Å; O(1)−C(3), 1.27(2) Å; O(2)−C(4), 1.30(2) Å; O(2)−Sn(1)−O(2′), 94.5(4)°; O(1)−Sn(1)−O(2′), 81.4(3)°; O(1)−Sn(1)−O(2), 74.8(3)°; O(1)−Sn(1)−O(1′), 144.6(4)°.

of hinokitiol in **4a** [O(1)−Zn−O(2), 78.63(5)°; O(3)−Zn−O(4), 76.35(4)°] and the angles within the Zn_2O_2 rhombus at the center of the dimer [O(4)−Zn−O(4′), 73.54(5)°; Zn(1)−O(4)−Zn(1′), 106.46(5)°] closely replicate data for **3**. The octahedral coordination about zinc in **4a** is slightly more regular than that in **3** as a result of the flexible disposition of the monodentate ethanol in comparison to that of the second bridging tropolone in **3**. This difference is most clearly manifest in the *trans*-O(4′)−Zn−O(5) angle of 160.74(4)° [cf. **3**: ∠O(3)−Zn−O(4′), 147.81-(7)°]. Perhaps the most significant difference between the two structures is the dominance of chelation over bridging in **4a** and the intermolecular Zn−O(4′) bond [2.171(1) Å] which is significantly weaker than corresponding bonds in **3** [Zn−O(2′), 2.121 Å; Zn−O(4′), 2.103(2) Å]. The C(11)−O(4) bond [1.306-(2) Å] is elongated as a result of the dual bonding role for O(4), but O(4) still forms a stronger bond to Zn [2.075(1) Å] than the carbonyl oxygen, O(3) [Zn−O(3), 2.107(1) Å]. That is, the correlation of C−O/C=O and Zn−O bond lengths follows the expected pattern, and this is endorsed in the purely chelating ligand contained in **4a** based on O(1)/O(2) [C(1)=O(1), 1.277-(2) Å, Zn−O(1), 2.074(1) Å; C(2)−O(2), 1.287(2) Å, Zn−O(2), 2.029(1) Å].

For comparison, the structure of **1** has recently been reported[15] and we have independently determined identical crystallographic parameters as part of our work. Interestingly, unlike **3** and **4a**, compound **1** consists of two five-coordinate $Zn(malt)_2 \cdot H_2O$ moieties sandwiching a six-coordinate $Zn(malt)_2 \cdot 2H_2O$ unit in a triple-decker arrangement.

Both tin compounds **5** and **7** yielded poor quality crystals with pronounced platelike shapes. Despite this, the gross structural features of each could be determined, and both structures are remarkably similar. Both adopt pseudo-five-coordinate SnO_4E (E = lone pair), which are probably best described in terms of a trigonal bipyramidal geometry with one equatorial site occupied by a stereochemically active lone electron pair (Figures 3 and 4). There is, however, severe distortion from a regular polyhedron in both cases. Both maltol and tropolone chelate tin in an anisobidentate manner, with one short [**5**, Sn(1)−O(2), 2.129(8) Å; **7**, Sn(1)−O(1), 2.140(9) Å, Sn(1)−O(4), 2.140(10) Å] and one long [**5**, Sn(1)−O(1), 2.324-(8) Å; **7**, Sn(1)−O(2), 2.258(10) Å, Sn(1)−O(3), 2.242(10) Å]
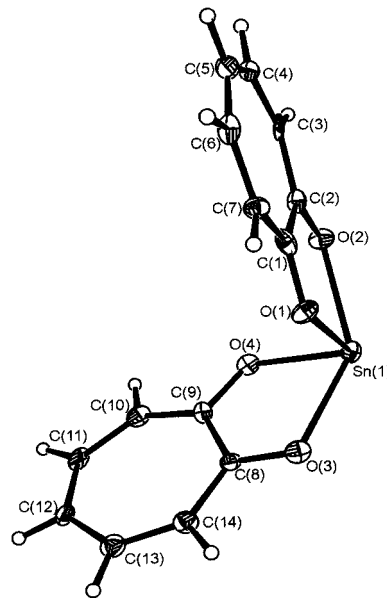

Figure 4. The structure of **7** highlighting the asymmetric unit and the labeling scheme used. Thermal ellipsoids are at the 30% probability level. Selected metrical data are as follows: Sn(1)−O(1), 2.140(9) Å; Sn(1)−O(2), 2.258(10) Å; Sn(1)−O(3), 2.242(10) Å; Sn(1)−O(4), 2.140(10) Å; C(1)−O(1), 1.27(2) Å; O(2)−C(2), 1.29(2) Å; O(3)−C(8), 1.26(2) Å; O(4)−C(9), 1.31(2) Å; O(1)−Sn(1)−O(2), 72.5(3)°; O(1)−Sn(1)−O(3), 77.1(4)°; O(1)−Sn(1)−O(4), 94.2(4)°; O(2)−Sn-(1)−O(3), 137.4(4)°; O(2)−Sn(1)−O(4), 81.1(4)°; O(3)−Sn(1)−O(4), 72.0(3)°.

bond to the metal; tropolone is marginally the more symmetrical of the two ligands in this respect. The Sn−O bonds in both compounds are longer than those in their dihalotin(IV) analogues $F_2Sn(malt)_2$,[8] $Cl_2Sn(malt)_2$,[23] and $Cl_2Sn(trop)_2$,[23] presumably reflecting the increased Lewis acidity at tin in these examples which arises from the presence of electronegative halogens attached to the metal. The "bite" angles for the two tropolone ligands in **7** [∠O(1)−Sn(1)−O(2), 72.5(3)°; ∠O(3)−Sn(1)−O(4), 72.0(3)°] are smaller than those in the zinc analogue (**3**) and the maltolate (**5**) [∠O(1)−Sn(1)−O(2), 74.8(3)°]. These bite angles distort the nominally axial ∠O−Sn−O significantly from the ideal 180° [**5**, ∠O(1)−Sn(1)−O(1′), 144.6(4)°; **7**, ∠O(2)−Sn(1)−O(3), 137.4(4)°].

We are unaware of any open-chain α-hydroxyketone derivatives of tin whose structures have been determined and could be compared with **5** and **7**. The structure of $Sn(oxalate)_2$ is, however, available and contains a similar local coordination sphere about tin, though as part of a polymeric structure.[24,25]

Supporting Information Available: X-ray crystallographic files in CIF format for $Zn(trop)_2$, $Zn(hino)_2 \cdot EtOH$, $Sn(malt)_2$, $Sn(trop)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

(23) Denekamp, C. I. F.; Evans, D. F.; Slawin, A. M. Z.; Williams, D. J.; Wong, C. Y.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1992**, 2375.
(24) Christie, A. D.; Howie, R. A.; Moser, W. *Inorg. Chim. Acta* **1979**, *36*, L447.
(25) Gleizes, A.; Galy, J. *J. Solid State Chem.* **1979**, *30*, 23.