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Crystallographic report

Diphenylbis(Hpiroxicam)tin(IV), [$Ph_2Sn(Hpir)_2$]

Dimitra Kovala-Demertzi[1]*, Aglaia Koutsodimou[1], Angeliki Galani[1], Sotiris K. Hadjikakou[1], Mavroudis A. Demertzis[1], Marianna Xanthopoulou[1], John R. Miller[2] and Christopher S. Frampton[3]**

[1] Inorganic and Analytical Chemistry, Department of Chemistry, University of Ioannina, 45100 Ioannina, Greece
[2] Department of Biological and Chemical Sciences, Central Campus, Wivenhoe Park, Colchester CO4 3SQ, UK
[3] Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

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The crystal structure of complex [$Ph_2Sn(Hpir)_2 \cdot CH_3CN$] shows for the first time chelation to a metal atom of piroxicam through the keto-enolate oxygen atoms. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: piroxicam; diphenyltin; structure; anti-inflammatory drug

COMMENT

The structure of [$Ph_2Sn(Hpir)_2 \cdot CH_3CN$] (Fig. 1) has an approximate (non-crystallographic) twofold axis through the tin atom and between the phenyl groups. The tin atom is coordinated in a very distorted octahedral configuration through its enolate and amide oxygen atoms in a *trans*-$O_{enolate}$-*cis*-O_{amide}-*cis*-C_2 configuration. The two phenyl groups are cis but the C–Sn–C angle is much greater than 90°; indeed, it is closer to the tetrahedral value. This large C–Sn–C angle demonstrates that the phenyl groups exert a very significant steric effect on each other and on the positions of the (Hpir) ligands. The drug, with four potential donor atoms and several possible isomers, is known to react as a monodentate ligand, through the pyridyl nitrogen towards platinum(II),[1,2] and as a singly deprotonated bidentate chelate ligand, through the pyridyl nitrogen and the amide oxygen towards copper(II) and cadmium(II).[3] In the present structure, the amide nitrogen atoms N(2) and N(5) remain protonated, as they are not coordinated. This is in sharp contrast to the behaviour of piroxicam with di-*n*-butyltin, which forms [$Bu_2Sn(pir)]_n$ with doubly deprotonated, tridentate piroxicam.[4]

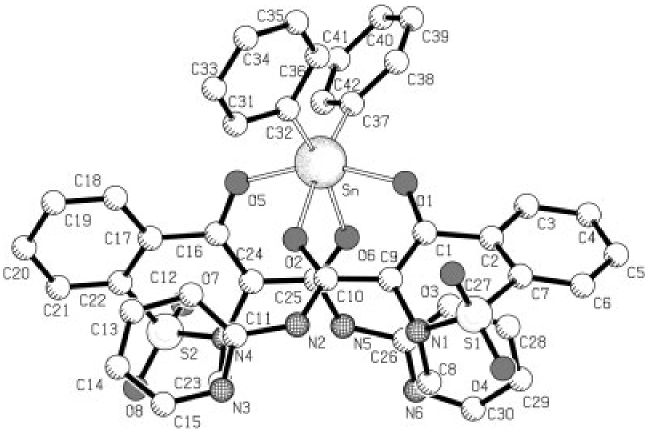

Figure 1. Molecular structure of [$Ph_2Sn(Hpir)_2$]. Key geometrical parameters: Sn–O1 2.103(4), Sn–O2 2.182(4), Sn–O5 2.107(4), Sn–O6 2.207(4), Sn–C31 2.142(7), Sn–C37 2.136(6) Å; O1–Sn–O2 81.4(2), O5–Sn–O6 80.2(2), O1–Sn–O5, 154.8(2), C31–Sn–C37 107.4(2)°.

EXPERIMENTAL

A suspension of H_2pir (0.332 g, 1 mmol) in distilled water (12 ml) was treated with a standard aqueous 0.1 mol dm^{-3} KOH solution (1 ml, 1.0 mmol). The resulting colourless solution was stirred while a solution of Ph_2SnCl_2 (0.152 g, 0.5 mmol) in methanol (6 ml) was added to give a colourless solution. The resulting powder was filtered off, washed with 5 ml of cold distilled water and

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*Correspondence to: Dimitra Kovala-Demertzi, Inorganic and Analytical Chemistry, Department of Chemistry, University of Ioannina, 45100 Ioannina, Greece.
E-mail: dkovala@cc.uoi.gr
**Correspondence to: Mavroudis A. Demertzis, Inorganic and Analytical Chemistry, Department of Chemistry, University of Ioannina, 45100 Ioannina, Greece.
E-mail: dkovala@cc.uoi.gr

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dried *in vacuo* over silica gel. Crystals of $[Ph_2Sn(Hpir)_2 \cdot CH_3CN]$ were obtained by slow evaporation of a fresh MeOH–MeCN solution. Intensity data were collected at 123 K on a Bruker SMART 1 K CCD diffractometer equipped with an Oxford Cryosystems Cryostream cooler for a needle-like crystal $0.05 \times 0.07 \times 0.30$ mm^3. $C_{43}H_{35.5}N_{6.5}O_8S_2Sn$, $M = 954.09$, monoclinic space group $P2_1/c$, $a = 13.182(4)$, $b = 12.910(6)$, $c = 25.475(11)$ Å, $\beta = 99.28(5)°$, $V = 4279(3)$ Å^3, $Z = 4$, $D_x = 1.481$ g cm^{-3}, $R = 0.069$ (5770 reflections with $I > 2\sigma(I)$), $wR = 0.170$ (all data), $\rho_{max} = 1.88$ e$^-$ Å^{-3}. The extreme anisotropy in the thermal parameters of the solvent atoms N(7) and C(44) also indicates a high degree of disorder in the lattice solvent. Programs used: SAINT V4.05, SADABS, SHELXL-97, PLATON. CCDC deposition number: 191259.

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