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Crystal structure of zinc[bis[3-(dimethylamino)propyl-*C*,*N*]tin]bis(dibenzoylmethanato)-(*Sn–Zn*). The first example of a dialkyltin(II) compound stabilized by Sn–Zn coordination

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Abstract

Reaction of bis[3-(dimethylamino)propyl]zinc with bis(dibenzoylmethanato)tin(II) affords novel zinc[bis[3-(dimethylamino)propyl-*C*,*N*]tin]bis(dibenzoylmethanato)-(*Sn–Zn*) (**1**) in a quantitative *trans*-metallation. The crystal structure of **1** has been determined by X-ray diffraction methods and reveals it to be a unique complex in which an intramolecularly coordinated dialkyltin(II) compound is acting as an electron donor to a zinc-β-diketonate acceptor molecule. The geometries about both tin and zinc are distorted trigonal bipyramidal and the donor Sn–Zn bond (2.634(6) Å) occupies an equatorial position in each array. The 3-(dimethylamino)propyl groups are *C*,*N*-chelate bonded to Sn, with C(1) atoms at equatorial sites (C–Sn–C 104(1)°) and the nitrogen atoms at axial sites (N–Sn–N 161.8(8)°).

The isolation and characterization of the title compound shows that dialkyltin(II) compounds can be stabilized by coordination to zinc-β-diketonates provided that (i) the zinc compound has appropriate acceptor properties and (ii) the alkyl groups bound to tin contain potential ligating functional groups.

Introduction

Recently, we and others have shown that it is possible to stabilize divalent organotin compounds through intramolecular coordination of a heteroatom-containing substituent. Examples are bis[8-(dimethylamino)-1-naphthyl]tin(II) [1], bis{[2-dimethylamino)methyl]phenyl}tin(II) [2] and bis[(2-pyridyl)bis(trimethylsilyl)-methyl]tin(II) [3]. In the first two compounds the geometry at tin can be described as ψ-trigonal bipyramidal, with the tin–carbon bonds and the Sn lone pair at the equatorial sites and the two nitrogen atoms at the axial positions. In the third compound the geometry at tin is square pyramidal, probably as a result of strain in the molecule caused by the presence of a four-membered chelate ring.

Another approach to the stabilization of divalent organotin compounds involves coordination of the tin atom, via its lone pair, to a suitable transition metal. Numerous compounds of this type are known and they have been reviewed recently [4]. Although adducts of dicyclopentadienyltin(II) with main-group Lewis acids such as AlX_3 and BX_3 ($X = F$, Cl, Br) are known [5–7], it is surprising that no other stannylenes show such reactivity [8].

Because of our interest in the relation between the flexibility of the chelate ring in divalent- [1,9,10] and tetravalent- [11–14] organotin compounds with heteroatom-containing substituents and the configurational stability of these compounds, we have studied the synthesis of a divalent organotin compound containing the 3-(dimethylamino)propyl group. In the case of intramolecular coordination, the resulting chelate ring would contain exclusively sp^3-hybridized atoms.

Results and discussion

When bis[3-(dimethylamino)propyl]zinc was treated with bis(dibenzoylmethanato)tin(II), $Sn(DBM)_2$, in a 1 : 1 molar ratio in benzene, a yellow solution was obtained. A crystalline product, analyzed as $Zn(DBM)_2Sn[(CH_2)_3NMe_2]_2$ (**1**), was obtained in quantitative yield by precipitation with n-pentane. The ^1H and ^{13}C NMR spectra of **1** in C_6D_6 showed the presence of both dimethylaminopropyl and DBM moieties, but it was not clear whether or not transmetallation of groups had taken place. As only indirect evidence for transmetallation from zinc to tin could be obtained (vide infra), it was decided to determine the solid-state structure of product **1**.

Compound **1** appears to be a unique species in which an intramolecularly coordinated dialkyltin(II) compound is acting as an electron donor to a zinc-β-diketonate acceptor. As a requirement of the space group symmetry the molecule has two fold axial symmetry along the Sn–Zn axis. The molecular geometry of $Zn(DBM)_2(Sn[(CH_2)_3NMe_2]_2)$ is shown in Fig. 1, and selected geometrical data are given in Table 1.

As a result of intramolecular Sn–N coordination the tin atom in **1** is pentacoordinate. The coordination geometry at tin is best described in terms of a distorted trigonal bipyramid, with the C–Sn bonds and the Zn atom at the equatorial sites and the more electronegative nitrogen atoms at the axial positions. The N–Sn–C angles (77(1)°) in the five-membered chelate rings deviate considerably from the ideal value for a trigonal bipyramid (90°), which is not unexpected as these angles are determined by the fairly inflexible values of the Sn–C and Sn–N bonding distances (see ref. 1 and references cited therein). Furthermore, relatively large values of the C–Sn–Zn angles (127(1)°) and the small C–Sn–C angle (104(1)°) are probably caused by mutual repulsion of the bulky $Zn(DBM)_2$ moiety and the $Sn[(CH_2)_3NMe_2]_2$ unit. The overall structural geometry around tin (bond distances and angles) of **1** is close to that reported for tungsten[bis[8-(dimethylamino)-1-naph-

Table 1

Selected geometrical data for **1**

bond distances (Å)			
Sn–Zn	2.634(6)	O(1)–C(7)	1.24(4)
Sn–N	2.49(3)	O(2)–C(9)	1.30(3)
Sn–C(16)	2.15(4)	N–C(18)	1.44(4)
Zn–O(1)	2.07(2)	N–C(19)	1.42(4)
Zn–O(2)	2.00(2)	N–C(20)	1.52(4)
bond angles (deg)			
Zn–Sn–N	99.1(6)	O(1)–Zn–O(1′)	163.1(7)
Zn–Sn–C(16)	128(1)	O(1)–Zn–O(2)	84.1(8)
N–Sn–N′	161.8(8)	O(1)–Zn–O(2′)	88.1(8)
N–Sn–C(16)	77(1)	O(2)–Zn–O(2′)	124.9(7)
N–Sn–C(16′)	92(1)	Zn–O(1)–C(7)	126(2)
N′–Sn–C(16)	92(1)	Zn–O(2)–C(9)	126(2)
C(16)–Sn–C(16′)	104(1)	Sn–N–C(18)	101(2)
Sn–Zn–O(1)	98.5(5)	Sn–N–C(19)	110(2)
Sn–Zn–O(2)	117.5(5)	Sn–N–C(20)	110(2)

thyl-*C*,*N*]tin]pentacarbonyl-(*Sn*–*W*) [1] and tungsten[bis[2-[(dimethylamino)methyl]phenyl-*C*,*N*]tin]pentacarbonyl-(*Sn*–*W*) [15].

The coordination geometry at zinc in **1** is also close to trigonal bipyramidal, as reflected in the sum of the bond angles in the equatorial plane (359.9°) defined by Sn, Zn, O(2) and O(2′), and O(1) and O(1′) are in the axial positions. A similar coordination geometry at zinc has been found in aquobis(acetylacetonato)zinc, [16] although the coordination geometry at zinc in the related ethanolbis(benzoylacetonato)zinc complex is square pyramidal, with the oxygen atom of the ethanol molecule at the apex of a square pyramid [17].

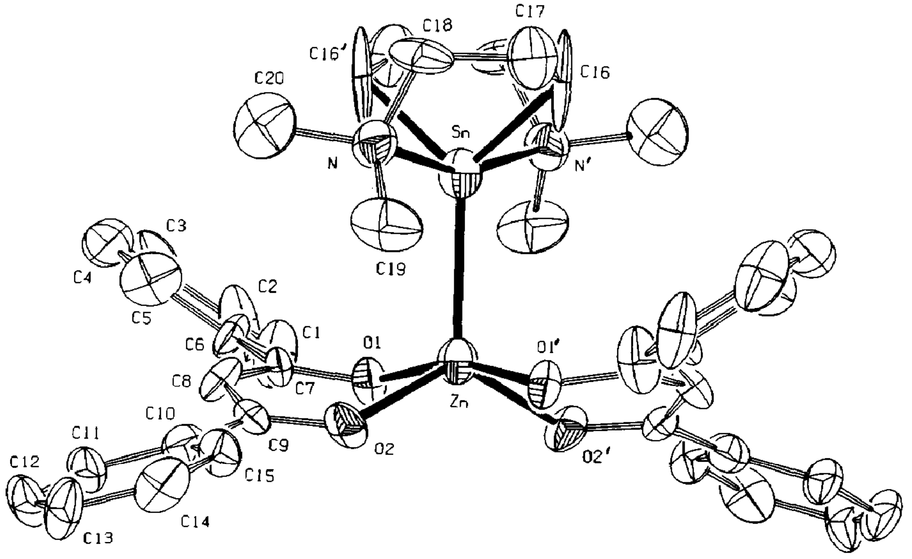
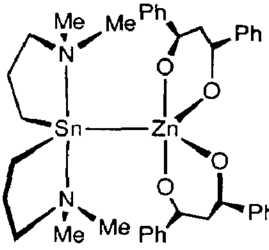


Fig. 1. ORTEP drawing (30 % probability level) of **1**, with the adopted numbering scheme. Primed atoms are related by the symmetry operation $-x$, y, $\frac{1}{2}-z$.

A molecular weight determination (ebulliometry in benzene) reveals that **1** is monomeric in benzene. The solid-state structure of **1** is probably retained in solution. Indications are the observation of very complex resonance patterns for the prochiral methylene resonances of the 3-(dimethylamino)propyl group in its ^1H NMR spectrum. Furthermore, two resonances are observed for the NMe_2 group in the ^1H (δ 2.05 and 2.50) and ^{13}C (δ 45.6 and 46.4) NMR spectra at low temperature (−20 °C), indicating that at this temperature Sn–N coordination is rigid on the NMR time scale. At higher temperatures (30 °C in the ^1H NMR spectrum, 0 °C in the ^{13}C NMR spectrum) these resonances coalesce, probably as the result of Sn–N dissociation/association processes.

The importance of the coordination of the $Sn[(CH_2)_3NMe_2]_2$ tin lone pair to the $Zn(DBM)_2$ moiety for the stability of **1** becomes evident when **1** is treated with one equivalent of tetramethylethylenediamine (TMEDA), (eq. 1). This reaction results in the quantitative formation of insoluble $Zn(DBM_2)(TMEDA)$ and a soluble organotin oligomer. It is clear that $Sn[(CH_2)_3NMe_2]_2$ is liberated by a ligand-substitution reaction and undergoes the fast oligomerization reaction that is common for simple dialkyl- and diaryltin compounds [18].



1

$$\xrightarrow{\text{TMEDA}} [SnR_2]_n + Zn(DBM)_2(TMEDA)\downarrow \quad (1)$$

$$R = -(CH_2)_3NMe_2$$

That intramolecular Sn–N coordination also contributes to the stability of **1** is suggested by the observation that the transmetallation reaction of diethylzinc with $Sn(DBM)_2$ gives $Zn(DBM)_2$ and diethyltin, which was isolated as an oligomeric oil, eq. 2.

$$Sn(DBM)_2 + Et_2Zn \longrightarrow -[SnEt_2]_n- + Zn(DBM)_2 \quad (2)$$

Experimental

Syntheses were carried out by standard Schlenk techniques under purified nitrogen. The solvents were dried and distilled from sodium prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. Bis[3-(dimethylamino)propyl]zinc [19] and bis(dibenzoylmethanato)tin(II) [20] were prepared by published procedures.

Synthesis of zinc[bis[3-(dimethylamino)propyl-C,N]tin]bis(dibenzoylmethanato)-(Sn–Zn) (1)

To a solution of bis(dibenzoylmethanato)tin(II) (1.65 g, 2.92 mmol) in benzene (20 mL) was added a solution of bis[3-(dimethylamino)propyl]zinc (0.70g, 2.95 mmol) in benzene (10 mL). The resulting yellow solution was stirred for 2 h and the solvent was then removed in vacuo. The residual yellow solid was washed with two

25 mL portions of pentane and dried in vacuo, to give pure **1** as a yellow solid (yield 1.41 g, 60%).

Anal. Found: C, 58.42; H, 5.71; N, 3.26; O, 8.22; MW 770 (cryoscopy in C_6H_6). $C_{40}H_{46}N_2O_4SnZn$ calcd.: C, 59.99; H, 5.54; N, 3.50; O, 7.99%; MW 801. ^{1}H NMR (CD_2Cl_2, $-20\,^\circ$C) δ 2.05 and 2.50 (both 3H, NMe_2), 0.70 and 0.95 (both 1H, α-CH_2), 6.68 (1H, CH(DBM)), 7.40 and 7.95 (10H, aromatics). ^{13}C NMR (CD_2Cl_2, $-20\,^\circ$C) δ 62.3 (NCH_2), 45.6 and 46.4 (NMe_2), 24.7 (β-CH_2), 16.6 (α-CH_2), 185.4 (C=O), 141.1, 130.4, 128.1 and 127.1 (aryl), 92.6 (CH-(DBM)).

Reaction of 1 with TMEDA

Pure TMEDA (0.3 g, 2.6 mmol) was added to a solution of **1** (2.05 g, 2.6 mmol) in benzene (10 mL). A white precipitate immediately separated. The mixture was stirred for 1 h and then 20 mL of pentane was added. The solid was filtered off, washed with pentane, and dried in vacuo, to give 1.55 g $Zn(DBM)_2(TMEDA)$ as an off-white crystalline solid (yield 95%).

Anal. Found: C, 68.60; H, 6.14; N, 4.41. $C_{36}H_{38}N_2O_4Zn$ calcd.: C, 68.84; H, 6.10; N, 4.46%.

The filtrate was evaporated under reduced pressure to give a viscous yellow oil, which from the broad resonances in its ^{1}H and ^{13}C NMR spectra is probably an organotin oligomer.

Reaction of $Sn(DBM)_2$ with Et_2Zn

To a solution of bis(dibenzoylmethanato)tin(II) (1.20 g, 2.12 mmol) in benzene (20 mL) was added a solution of diethylzinc (0.26 g, 2.12 mmol) in hexane (5 mL). The resulting dark solution was stirred for 1 h, and then 20 mL of pentane was added. The solid formed was filtered off, washed with pentane, and dried in vacuo, to give pure $Zn(DBM)_2$ as a pale yellow solid (yield 1.0 g, 93%).

Anal. Found: C, 70.45; H, 4.39; O, 12.41. $C_{30}H_{22}O_4Zn$ calcd.: C, 70.39; H, 4.33; O, 12.50%.

Evaporation of the filtrate yielded the diethyltin oligomer as a dark viscous oil, which was not further studied.

Crystal structure determination of 1

Transparant yellow crystals of **1**, grown from benzene, are monoclinic, space group $C2/c$ with four molecules in a unit cell of dimensions $a = 24.79(2)$, $b = 8.15(1)$, $c = 20.87(3)$ Å, $\beta = 115.2(1)\,^\circ$, $V = 3815$ (8) Å^3 ($F(000) = 1648$; $d_x = 1.398$ g cm^{-3}, $\mu = 13.4$ cm^{-1}). X-ray data were collected for a plate shaped crystal ($0.05 \times 0.25 \times 0.58$ mm) mounted in a Lindemann glass capillary (CAD4F; Mo-K_α, $\lambda = 0.71069$ Å; $\theta < 25\,^\circ$; $\omega/2\theta$ scan; $\Delta\omega = 1.30 + 0.35$ tg $\theta\,^\circ$; 3202 unique reflections). The crystals reflected poorly; reflection profiles were broad and structured, and the crystal decayed during data collection to 30%. The structure was solved by Patterson methods (SHELXS-86) [21] and refined with weighted full-matrix least-squares (SHELX-76) [22] to $R = 0.099$ ($R_w = 0.13$; $w^{-1} = \sigma^2(F) + 0.0005F^2$; 227 parameters; 1030 reflections with $I > 2.5\ \sigma(I)$; non-H atoms anisotropic; H atoms on calculated positions). Scattering factors were taken from ref. 23 and corrected for anomalous dispersion [24]. Calculations were carried out on a microVax-cluster. Coordinates of the non-hydrogen atoms are given in Table 2. Complete tables of

Table 2

Final coordinates and equivalent isotropic thermal parameters and their esds in parentheses for the non-H atoms of **1**

Atom	x	y	z	U_{eq} Å$^{2\,a}$
Sn	0	1.1305(4)	1/4	0.063(1)
Zn	0	0.8073(5)	1/4	0.062(2)
O(1)	0.0712(8)	0.770(2)	0.225(1)	0.064(8)
O(2)	−0.0468(8)	0.694(2)	0.158(1)	0.065(8)
N	−0.100(1)	1.179(3)	0.150(1)	0.07(1)
C(1)	0.176(1)	0.815(4)	0.211(2)	0.09(2)
C(2)	0.226(2)	0.867(5)	0.209(2)	0.11(2)
C(3)	0.225(2)	0.963(5)	0.154(2)	0.12(2)
C(4)	0.169(2)	1.002(4)	0.098(2)	0.10(2)
C(5)	0.120(1)	0.941(4)	0.105(2)	0.09(1)
C(6)	0.121(1)	0.845(4)	0.157(2)	0.06(1)
C(7)	0.071(1)	0.793(3)	0.166(2)	0.06(1)
C(8)	0.017(1)	0.770(3)	0.105(1)	0.06(1)
C(9)	−0.038(1)	0.706(3)	0.101(1)	0.05(1)
C(10)	−0.089(2)	0.657(3)	0.034(1)	0.07(1)
C(11)	−0.082(1)	0.610(3)	−0.024(1)	0.07(1)
C(12)	−0.131(2)	0.553(4)	−0.084(1)	0.08(1)
C(13)	−0.185(2)	0.541(4)	−0.085(2)	0.10(1)
C(14)	−0.193(1)	0.585(4)	−0.025(2)	0.09(1)
C(15)	−0.146(1)	0.643(3)	0.033(1)	0.07(1)
C(16)	−0.043(1)	1.292(5)	0.296(2)	0.14(2)
C(17)	−0.106(2)	1.330(4)	0.248(2)	0.09(2)
C(18)	−0.117(1)	1.331(3)	0.172(2)	0.09(1)
C(19)	−0.137(1)	1.041(4)	0.142(2)	0.11(2)
C(20)	−0.092(2)	1.207(5)	0.082(2)	0.12(2)

[a] $U_{eq} = \frac{1}{3}\Sigma\Sigma U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

atomic coordinates and bond distances and angles, and lists of thermal parameters and structure factors are available from ALS.

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References

1 J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, D. Heijdenrijk, K. Goubitz and D.J.A. de Ridder, J. Organomet. Chem., 367 (1989) 55.

2 K. Angermund, K. Jonas, C. Krüger, J.L. Latten and Y.-H. Tsay, J. Organomet. Chem., 353 (1988) 17.

3 L.M. Engelhardt, B.S. Jolly, M.F. Lappert, C.L. Raston and A.H. White, J. Chem. Soc., Chem., Commun., (1988) 336.

4 M.S. Holt, W.L. Wilson and J.H. Nelson, Chem., Rev., 89 (1989) 11.

5 P.G. Harrison and J.J. Zuckerman, J. Am. Chem. Soc., 92 (1970) 2577.

6 J. Doe, S. Borkett and P.G. Harrison, J. Organomet. Chem., 52 (1973) 343.

7 P.G. Harrison and J.A. Richards. J. Organomet. Chem., 108 (1976) 35.

8 J.D. Cotton, P.J. Davidson and M.F. Lappert, J. Chem. Soc., Dalton Trans., (1976) 2275.

9 J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, M.C. Zoutberg and D. Heijdenrijk, Organometallics, 8 (1989) 1373.

10 J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma and G. van Koten, Recl. Trav. Chim., Pays-Bas, submitted.

11 G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F. Pontenagel, J. Kroon and A.L. Spek, J. Am. Chem. Soc., 100 (1978) 5021.

12 G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, G.J. Verhoeckx, A.L. Spek and J. Kroon, J. Chem. Soc., Dalton Trans., (1980) 1382.

13 J.T.B.H. Jastrzebski, C.T. Knaap and G. van Koten, J. Organomet. Chem., 255 (1983) 287.

14 J.T.B.H. Jastrzebski, G. van Koten, C.T. Knaap, A.M.M. Schreurs, J. Kroon and A.L. Spek, Organometallics, 5 (1986) 1551.

15 H.-P. Abicht, K. Jurkschat, A. Tzschach, K. Peters, E.-M. Petres and H.G. von Schnering, J. Organomet. Chem., 326 (1987) 357.

16 E.L. Lippert and M.R. Trutter, J. Chem. Soc., (1960) 4996.

17 R.L. Belford, N.D. Chasteen, M.A. Hitchman, P.-K. Hon, C.E. Pfluger and I.C. Paul, Inorg. Chem., 8 (1969) 1312.

18 M. Veith and O. Recktenwald, Curr. Chem., 104 (1982) 1.

19 H.K. Hofstee, J. Boersma, J.D. van der Meulen and G.J.M. van der Kerk, J. Organomet. Chem., 153 (1978) 245.

20 A.B. Coernwell and P.G. Harrison, J. Chem. Soc., Dalton Trans., (1975) 1722.

21 G.M. Sheldrick, SHELXS86 (1986), Program for crystal structure determination, Univ. of Göttingen, Federal Republic of Germany.

22 G.M. Sheldrick, SHELX76 (1976), Program for crystal structure determination, Univ. of Cambridge, England.

23 D.T. Cromer and J.B. Mann, Acta Cryst. A, 24 (1968) 321.

24 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.