Oxidative Addition of Tetraethylthiuram Disulfide to Tin(II) Catecholate: X-Ray and Theoretical Investigations

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The reaction of tin(II) catecholate with tetraethylthiuram disulfide yields the addition product $(o\text{-}C_6H_4O_2)Sn[S_2CN(C_2H_5)_2]_2$, whose structure has been elucidated by X-ray crystallography, as a rare neutral tris chelate of tin(IV).

The oxidative addition of several addenda to tin(II) catecholate is known.[6] However, diphenyl disulfide was reported not to undergo oxidative addition with tin(II) catecholate.[6] This prompted us to investigate the reactivity of the latter towards another disulfide, *viz*. tetraethylthiuram disulfide, a molecule capable of generating chelating dithiocarbamate fragments during oxidative addition. The results of our investigation are presented below.

A solution of TDS (3.64 mmol) in about 10 ml of methanol was added dropwise to a suspension of tin(II) catecholate (3.66 mmol) in methanol. The mixture was stirred for about 15 h, whence a clear solution was obtained. The solvent was then removed *in vacuo*. The resulting orange–red solid was washed with light petroleum (bp 40–60 °C) and dried under high vacuum. The product was soluble in chloroform, benzene and tetrahydrofuran. Yield: 1.1 g; mp 231 °C(d). A perspective view of the molecule along with the atom numbering scheme is given in Fig. 1. The tin atom has a distorted octahedral environment with two bidentate dithiocarbamato groups and one bidentate catecholato group. The PM3 energy minimized structure[22] yielded bond lengths and angles which agreed well with the experimental values. The thermodynamic stability of $(o\text{-}C_6H_4O_2)Sn[S_2CN(C_2H_5)_2]_2$ is revealed by its calculated heat of formation ($\Delta H_f = -30.97$ kcal mol^{-1}).

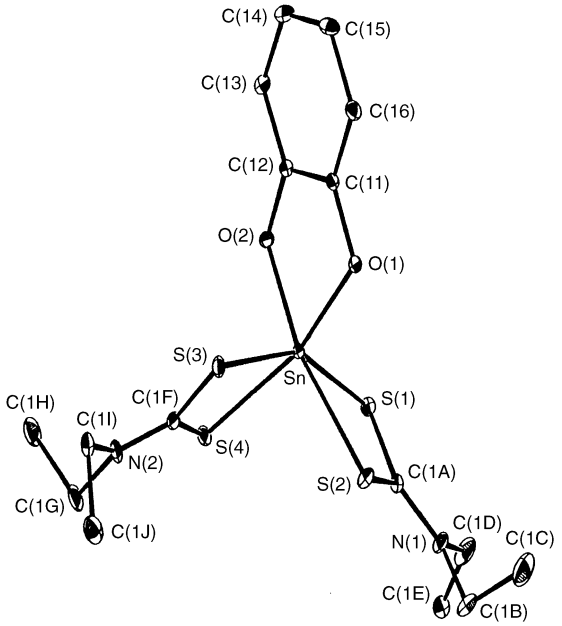

Fig. 1 Thermal ellipsoidal plot of $(o\text{-}C_6H_4O_2)Sn[S_2CN(C_2H_5)_2]_2$ with 30% probability of thermal ellipsoids. Bond lengths (Å) Sn–O(1) 2.033(5); Sn–O(2) 2.026(5); Sn–S(1) 2.541(3); Sn–S(2) 2.527(3); Sn–S(3) 2.548(2); Sn–S(4) 2.508(2). Bond angles (°) O(2)–Sn–O(1) 81.3(2); S(2)–Sn–S(1) 71.12(9); S(4)–Sn–S(3) 71.40(9)

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Some details and results of the crystallographic study are as follows. Empirical formula, $C_{16}H_{24}N_2O_2S_4Sn$; Formula M_r, 523.30; crystal colour/habit, orange–red/plates; temperature, 298(2) K; wavelength, $\lambda = 0.71069$ Å; crystal system, triclinic; space group, $P\bar{1}$; unit cell dimensions, $a = 9.759(1)$, $b = 10.391(4)$, $c = 13.199(1)$ Å; $\alpha = 95.63(6)$, $\beta = 105.77(2)$, $\gamma = 117.65(2)^\circ$; volume = 1101(1) Å^3; $Z = 2$; Density (cald) = 1.579 Mg m^{-3}; absorption coefficient = 1.552 mm^{-1}; $F(000) = 528$; θ range for data collection, 2.29–24.98°; index ranges $0 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 10$, $-15 \leqslant l \leqslant 15$; reflections collected, 4116; independent reflections 3866 [$R_{int} = 0.0279$]; refinement method, full-matrix least-squares on F^2; data/restraints/parameters 3866/0/227; goodness-of-fit on F^2, 1.087; final R indices [$I > 2\sigma(I)$], $R_1 = 0.0574$, $wR_2 = 0.1974$ (for 3474 data); R indices (all data) $R_1 = 0.0637$, $wR_2 = 0.2065$; largest diff. peak and hole 1.565 and −1.793 e Å^{-3}, respectively; radiation, graphite-monochromated Mo-Kα; scan method, 2θ. Additional crystal data can be found in the full text version.

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Techniques used: IR, ^{1}H and ^{119}Sn NMR, ^{119}Sn Mössbauer, mass spectrometry, single crystal X-ray diffraction

References: 22

Table 1: Crystal data and refinement parameters for $(o\text{-}C_6H_4O_2)Sn[S_2CN(C_2H_5)_2]_2$

Table 2: Selected bond lengths and angles for $(o\text{-}C_6H_4O_2)Sn[S_2CN(C_2H_5)_2]_2$ by X-ray and PM3 calculations

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