The isolation and structural characterization of dichloro[2,6-diacetylpyridinebis(semicarbazone)]tin(IV) dichloride dihydrate

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Abstract

The planar pentadentate ligand 2,6-diacetylpyridinebis(semicarbazone), DAPSC, was found to combine with $SnCl_3^-$ dissociated from $[Pt(SnCl_3)_5]^{3-}$ and form a pentagonal bipyramidal complex of Sn(IV). The complex was characterized by an X-ray crystal structure study. The $[Sn(DAPSC)Cl_2]\cdot 2H_2O$ complex crystallized in space group $P2_1/n$ with four molecules in a unit cell with dimensions $a = 9.213(2)$, $b = 13.391(4)$, $c = 16.856(7)$ Å and $\beta = 95.60(3)°$. The R and R_w values were 0.047 and 0.061, respectively for 2832 reflections. The cation is a slightly distorted pentagonal bipyramid in which the DAPSC ligand forms a pentagonal plane and two chloride ions occupy the axis positions. This is the first example of a metal oxidation taking place in the presence of DAPSC and being stabilized by the ligand.

Introduction

2,6 - diacetylpyridinebis(semicarbazone), DAPSC (Fig. 1), reacts with virtually all +2 and +3 ions of Groups 3, 12 and 13 as well as the elements Ti to Cu [1]. The usual result is pentagonal bipyramidal (PBP) geometry although higher coordination numbers are found with the larger +3 ions [2]. During investigations involving $(CH_4N)_3[Pt(SnCl_3)_5]$ (**I**), we unexpectedly isolated a PBP Sn(IV) complex from aqueous solution. Since there have been only three previous reports [3] of seven-coordinate Sn(IV) compounds involving planar pentadentate ligands, we take this opportunity to add to the relatively unexplored area of PBP Sn(IV).

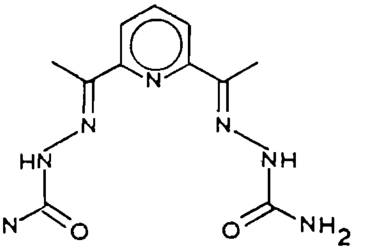

Fig. 1. The ligand DAPSC, 2,6-diacetylpyridinebis(semicarbazone).

Experimental

Preparation of $[Sn(DAPSC)Cl_2]Cl_2\cdot 2H_2O$

I (0.632 g) and DAPSC (0.113 g), both prepared by methods previously described [1c, 4], were slurried in 40 ml of H_2O. HCl was added dropwise until the pH = 1.00. As the solution cleared to a yellow–brown color, a fine black precipitate was evident in the solution. A dark yellow–brown solution void of black precipitate was obtained after filtering through a fine glass frit. Slow evaporation of the filtrate gave yellow crystals within four days.

X-ray crystallography

A crystal 0.15 × 0.17 × 0.23 mm suitable for diffraction studies was mounted on the end of a glass fiber. All subsequent measurements were made using a Nicolet P3m diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The cell dimensions were determined by a least-squares refinement of 25 automatically centered reflections. A variable-speed (1°–29.3°) 2θ scan technique was used to measure the intensity data from 0–50° in 2θ. Two standard reflections were measured every 98 reflections to

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TABLE 1. Crystal data

Formula	$SnC_{11}N_7O_4H_{19}Cl_4$
Molecular weight	573.81
a (Å)	9.213(2)
b (Å)	13.391(4)
c (Å)	16.856(7)
β (°)	95.60(3)
V (Å^3)	2069.6
Z	4
ρ_{calc} (g cm^{-3})	1.83
Space group	$P2_1n$
μ (cm^{-1})	87.2
No. of data used ($I_{net} > 2.5\sigma I_{net}$)	2832
R^a	4.7
$R_w{}^b$	6.1

$$^aR = \sum \frac{|F_o| - |F_c|}{|F_c|}; \quad ^bR_w = \left[\frac{\Sigma\, w(|F_o| - |F_c|)^2}{\Sigma\, w|F_o|^2}\right]^{1/2}$$

TABLE 2. Atomic parameters x, y, z and B_{iso} with e.s.d.s in parentheses[a]

	x/a	y/b	z/c	B_{iso}
Sn	0.7209(1)	0.8794(1)	0.1567(1)	2.011(21)
Cl1	0.7977(3)	0.7284(2)	0.2187(1)	3.31(10)
Cl2	0.6410(3)	1.0346(2)	0.1010(1)	3.14(9)
O1	0.5462(6))	0.8820(5)	0.2303(3)	2.67(24)
O2	0.5548(7))	0.8033(5)	0.0844(3)	2.09(3)
N3	0.8018(7)	0.9612(5)	0.2706(4)	2.1(3)
N4	0.9554(7)	0.9285(5)	0.1551(4)	2.1(3)
N5	0.8062(8)	0.8419(5)	0.0391(4)	2.2(3)
N1	0.4690(10)	0.9221(7)	0.3494(5)	3.5(4)
N2	0.6985(7)	0.9660(6)	0.3238(4)	2.6(3)
N6	0.7071(9)	0.8016(6)	−0.0146(4)	2.8(3)
N7	0.4779(10)	0.7322(7)	−0.0344(5)	3.3(4)
C1	0.5683(10)	0.9225(7)	0.2994(5)	2.5(3)
C2	0.9313(10)	0.9952(7)	0.2845(5)	2.6(3)
C3	0.9911(13)	1.0438(10)	0.3594(6)	3.8(5)
C4	1.0211(9)	0.9794(6)	0.2176(5)	2.3(3)
C5	1.1647(10)	1.0122(7)	0.2174(6)	3.0(4)
C6	1.2383(10)	0.9893(8)	0.1532(6)	3.4(4)
C7	1.1722(10)	0.9348(8)	0.0897(6)	3.0(4)
C8	1.0287(10)	0.9064(6)	0.0920(5)	2.5(3)
C9	0.9410(10)	0.8556(6)	0.0256(5)	2.3(3)
C10	1.0033(12)	0.8258(8)	−0.0488(6)	3.0(4)
C11	0.5773(10)	0.7790(6)	0.0140(5)	2.5(3)
C13	0.6830(3)	0.7146(2)	0.8170(1)	4.13(11)
C14	0.6672(3)	1.0786(2)	0.4759(1)	3.89(11)
W1	0.7343(10)	0.8522(7)	0.5155(5)	4.6(4)
W2	0.8857(11)	0.3283(8)	0.8452(6)	6.4(5)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid; e.s.d.s refer to the last digit printed.

TABLE 3. Bond distances and angles

Distances (Å)	
Sn–Cl(1)	2.3544(24)
Sn–Cl(2)	2.3681(24)
Sn–O(1)	2.127(5)
Sn–O(2)	2.123(6)
Sn–N(3)	2.272(7)
Sn–N(4)	2.260(7)
Sn–N(5)	2.259(6)
O(1)–C(1)	1.282(10)
O(2)–C(11)	1.267(10)
N(3)–N(2)	1.371(9)
N(3)–C(2)	1.277(12)
N(4)–C(4)	1.348(10)
N(4)–C(8)	1.347(10)
N(5)–N(6)	1.336(10)
N(5)–C(9)	1.297(11)
N(1)–C(1)	1.304(11)
N(2)–C(1)	1.360(12)
N(6)–C(11)	1.367(12)
N(7)–C(11)	1.322(12)
C(2)–C(3)	1.479(13)
C(2)–C(4)	1.477(12)
C(4)–C(5)	1.395(12)
C(5)–C(6)	1.368(14)
C(6)–C(7)	1.386(14)
C(7)–C(8)	1.381(13)
C(8)–C(9)	1.481(13)
C(9)–C(10)	1.484(12)
Angles (°)	
Cl(1)–Sn–Cl(2)	176.94(8)
Cl(1)–Sn–O(1)	88.07(19)
Cl(1)–Sn–O(2)	90.64(19)
Cl(1)–Sn–N(3)	88.79(19)
Cl(1)–Sn–N(4)	90.51(8)
Cl(1)–Sn–N(5)	94.78(19)
Cl(2)–Sn–O(1)	89.62(19)
Cl(2)–Sn–O(2)	90.86(19)
Cl(2)–Sn–N(3)	88.61(19)
Cl(2)–Sn–N(4)	90.03(18)
Cl(2)–Sn–N(5)	88.22(19)
O(1)–Sn–O(2)	78.38(22)
O(1)–Sn–N(3)	72.75(23)
O(1)–Sn–N(4)	141.35(23)
O(1)–Sn–N(5)	149.72(24)
O(2)–Sn–N(3)	151.13(23)
O(2)–Sn–N(4)	140.27(23)
O(2) Sn N(5)	71.46(24)
N(3)–Sn–N(4)	68.61(23)
N(3)–Sn–N(5)	137.34(25)
N(4)–Sn–N(5)	68.87(24)
Sn–O(1)–C(1)	118.3(5)
Sn–O(2)–C(11)	119.1(6)
Sn–N(3)–N(2)	112.5(5)
Sn–N(3)–C(2)	123.3(5)
N(2)–N(3)–C(2)	124.1(7)
Sn–N(4)–C(4)	119.6(5)
Sn–N(4)–C(8)	119.9(6)
C(4)–N(4)–C(8)	120.4(7)
Sn–N(5)–N(6)	114.3(5)
Sn–N(5)–C(9)	123.0(6)
N(6)–N(5)–C(9)	122.7(7)
N(3)–N(2)–C(1)	115.5(7)
N(5)–N(6)–C(11)	114.4(7)
O(1)–C(1)–N(1)	121.8(8)
O(1)–C(1)–N(2)	120.9(7)
N(1)–C(1)–N(2)	117.4(8)
N(3)–C(2)–C(3)	125.2(8)
N(3)–C(2)–C(4)	113.1(7)
C(3)–C(2)–C(4)	121.7(8)
N(4)–C(4)–C(6)	115.2(7)
N(4)–C(4)–C(5)	120.8(8)
C(2)–C(4)–C(5)	124.0(8)
C(4)–C(5)–C(6)	118.4(9)
C(5)–C(6)–C(7)	121.0(9)
C(6)–C(7)–C(8)	118.3(8)
N(4)–C(8)–C(7)	121.1(8)
N(4)–C(8)–C(9)	114.8(8)
C(7) C(8) C(9)	124.0(8)
N(5)–C(9)–C(8)	113.1(7)
N(5)–C(9)–C(10)	124.5(8)
C(8)–C(9)–C(10)	122.4(8)
O(2)–C(11)–N(6)	120.2(8)
O(2)–C(11)–N(7)	122.1(9)
N(6)–C(11)–N(7)	117.7(8)

monitor for any decomposition during the X-ray analysis. No absorption correction was made. The pertinent crystal data are given in Table 1.

Structure refinement

The data reduction, structure solution and final refinement were performed using the NRCVAX (PC-Version) [5] package of programs. The Sn atom and all non-hydrogen atoms were located by the heavy-atom method (Patterson and Fourier syntheses) and refined anisotropically by full-matrix least-squares. The hydrogen atoms were located using a difference Fourier map and refined isotropically. The model converged to an R of 0.047 and a R_w of 0.061. The final positional parameters are given in Table 2. The final bond distances involving the non-hydrogen atoms and bond angles are listed in Table 3.

Results and discussion

The crystals were found to contain monomeric $Sn(DAPSC)Cl_2{}^{2+}$ cations and display PBP geometry which is easily seen in Fig. 2. It is noteworthy that this complex was obtained from aqueous solution and is very water soluble since all related compounds [3] were isolated from organic media. Oxidation of Sn^{2+} to Sn^{4+} is known [6] to occur in aqueous solutions exposed to air and has been observed to occur in a structurally similar complex [3a]. Indeed, a similar oxidation has occurred in this instance. As noted above, a fine black precipitate fell out as the solution cleared which suggests that a reduction of the Pt^{2+} starting material to Pt^0 occurred. Whether or not this was a direct result of the Sn oxidation is not clear. This is the first example of a metal oxidation taking place in the presence of DAPSC and being stabilized by the ligand. DAPSC tends to have a more reducing nature as is observed in the Fe^{2+} and Co^{2+} systems [1a].

Compounds such as **I** and Pt(II)/Sn(II) mixtures have been of interest for some time due to the observed capability of these species to homogeneously catalyze the hydroformylation, carbonylation and hydrogenation reactions [6]. Common to most of the discussion regarding possible mechanisms for these reactions is the postulated presence of free $SnCl_3{}^-$ ions in solution liberated by ligand dissociation. Although it has been shown [7] that the $[Pt(SnCl_3)_5]^{3-}$ species has long-term stability in the absence of protic solvents, in HCl solutions stability is reduced greatly and metallic Pt is slowly precipitated as we observed. Hence, the concentration of free $SnCl_3{}^-$

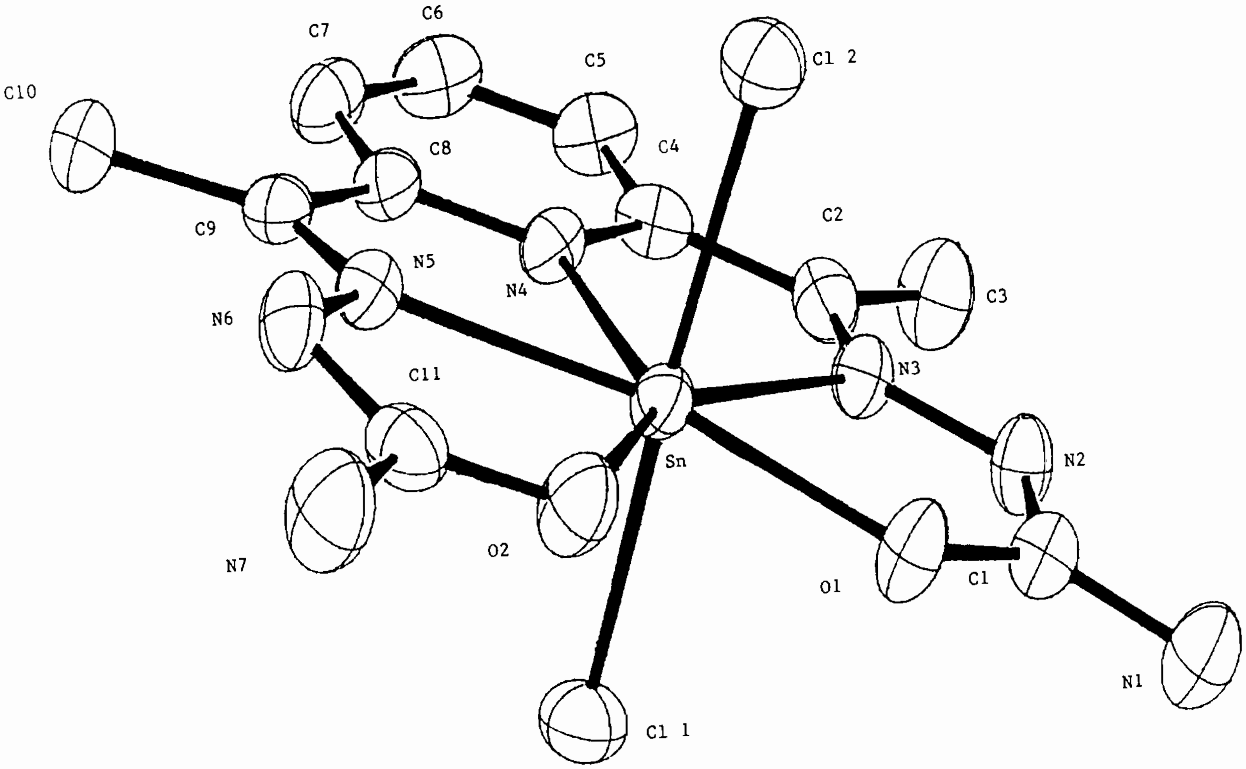

Fig. 2. An ORTEP representation of $[Sn(DAPSC)Cl_2]^{2+}$ with ellipsoids drawn at the 50% probability level.

is probably quite high in a HCl solution of compound **I** with pH = 1.00 and the likely source of the Sn atom for coordination by DAPSC. Attempts to prepare the title complex in good yield from $SnCl_2 \cdot 2H_2O$ and DAPSC from HCl and methanol/H_2O solutions failed even when excess halide was added in the form of KCl which promotes [8] the formation of $SnCl_3^-$.

The geometry about the Sn cation can be described as a slightly distorted pentagonal bipyramid. A slight distortion is apparent in the pentagonal equatorial plane as evidenced by the lengths of the respective sides: O1–O2, 2.685(7); O1–N3, 2.611(8); N3–N4, 2.553(9); N4–N5, 2.555(9); N5–O2, 2.560(9) Å. The axial chlorides also contribute to the observed distortion since they are not exactly linear and make an angle of 176.94(8)°. A least-squares plane drawn through the five coordinating atoms in the equatorial girdle shows little deviation from planarity with the average of the deviations being 0.034(7) Å. The Sn ion can be considered to lie in the equatorial plane since it deviates only 0.019(3) Å out of the plane made by the five equatorial donors. Dimensions within the neutral ligand are similar to those observed in related structures with no irregularities. There is evidence of several hydrogen bonds within the asymmetric unit. Most notable are the interactions between N2–C14, N6–C13 and N7–W1 with distances (H···Cl) of 2.053(10), 2.289(10) and 1.863(10) Å, and with bond angles of 152(1), 143(1) and 156(1)°, respectively.

The two Sn–Cl distances appear to be significantly different, $t_0 = 4.09$ [9], although they appear to be chemically equivalent. However an analysis of the various intermolecular contacts involving Cl1 and Cl2 indicates that the two Cl atoms have slightly different environments which could account for the small but significant difference. The Sn–Cl distances are slightly shorter than those of 2.395(7) and 2.387(7) Å found in $[Sn(dappc)Cl_2]^{2+}$ [3a]. However the Sn–O and Sn–N distances are slightly longer than in the $[Sn(dappc)Cl_2]^{2+}$ complex which suggests that the Sn–Cl distance may be influenced by non-bonded interactions. The much longer Sn–Cl bond distance of 2.446(3) Å when the *trans* atom is carbon suggests a *trans* influence may be operative in Sn compounds. The Sn–Cl distance of 2.362(4) Å in tris(tropolonato)monochlorotin(IV) chloroform solvate [10] would support this view. Unfortunately there are not a sufficient number of seven-coordinate Sn(IV) complexes for a detailed comparison. An analysis of the Sn–Cl distances in hexacoordinate Sn complexes is in progress.

Finally, it has been suggested [11] that tin in a seven-coordinate environment prefers pentagonal bipyramidal geometry; in our compound however, the result may be attributed to the planar pentadentate nature of the ligand rather than any stereochemical preference by the metal [12].

Supplementary material

Tables of anisotropic temperature factors, hydrogen atomic parameters and structure factors are available from the authors upon request.

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