Notes

The Crystal Structure of Diaquadichlorodimethyltin(IV)–Purine (1/4)†

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The structure of the compound $Sn(CH_3)_2Cl_2(H_2O)_2{\cdot}4C_5H_4N_4$ has been determined by single-crystal *X*-ray diffraction methods. The compound crystallizes in the monoclinic system, space group $P2_1/a$, with unit-cell dimensions $a = 11.218(4)$, $b = 18.374(5)$, $c = 7.193(3)$ Å, $\beta = 101.9(4)°$, and $Z = 2$. The structure is centrosymmetric at the all-*trans* $Sn(CH_3)_2Cl_2(H_2O)_2$ octahedral units, which are surrounded by four purine molecules hydrogen bonded to the H_2O ligands. Each purine also makes hydrogen bonds with purines adjacent to different $Sn(CH_3)_2Cl_2(H_2O)_2$ units to form a three-dimensional network. The purine molecules are present in tautomeric pairs: in one isomer a hydrogen atom is attached to the atom N(7) of the imidazole ring, as found in crystals of free purine, and in the other one to the atom N(9). Proton n.m.r. measurements on the system $Sn(CH_3)_2Cl_2$–purine in acetone show that also in solution direct co-ordination of the base to tin does not occur.

In the course of studies on the co-ordinating properties of organotin(IV) halides toward N-donor ligands we have isolated from solutions of dimethyltin dichloride and purine in moist acetone a compound which analyses as $Sn(CH_3)_2Cl_2(H_2O)_2{\cdot}4C_5H_4N_4$. This paper describes the crystal and molecular structure of the complex. Proton n.m.r. spectra of the system $Sn(CH_3)_2Cl_2$–purine in acetone solution are also reported. The structures of organotin(IV) hydrates and hydrolysates are a subject of interest in relation to the interaction of organotin(IV) species with biological systems in water.[1]

Experimental

Crystals of $Sn(CH_3)_2Cl_2(H_2O)_2{\cdot}4C_5H_4N_4$ were obtained by slow evaporation of solutions of $Sn(CH_3)_2Cl_2$ and purine (molar ratio 1:2) in commercial acetone. A well formed prismatic crystal of approximate dimensions 0.2 × 0.2 × 1 mm was mounted on a Philips PW 1100 diffractometer to determine the cell dimensions and to measure intensity data.

Crystal Data.—$C_{22}H_{26}Cl_2N_{16}O_2Sn$, $M = 736$, monoclinic, space group $P2_1/a$ (no. 14), $a = 11.218(4)$, $b = 18.374(5)$, $c = 7.193(3)$ Å, $\beta = 101.9(4)°$, $U = 1\,450.54$ Å^3, $Z = 2$, $D_c = 1.691$ g cm^{-3}, $F(000) = 736$.

Data Collection.—Data in the range $4 < 2\theta < 50°$ were collected by the θ–2θ step-scan method using Mo-K_α monochromatized radiation ($\lambda = 0.7107$ Å, $\mu = 10.16$ cm^{-1}). Reflections with $I > 3\sigma(I)$ were considered as observed (1 902 out of 2 559). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination and Refinement of the Structure.—The positions of the tin and chlorine atoms were obtained from a three-dimensional Patterson–Fourier synthesis. The remaining non-hydrogen atoms were located in a subsequent electron-density map. The hydrogen atoms were located from a Fourier difference map. Final refinements were carried out with anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The final conventional *R* factor was 0.037. The function minimized was $\Sigma w \Delta F^2$, with $w = 1/[\sigma^2(F) + 0.007F^2]$. Scattering factors for all atoms were those incorporated in the program SHELX.[2] Positional parameters of non-hydrogen atoms are listed in Table 1.

Proton N.M.R. Measurements.—Spectra were recorded on a Bruker WP 60 spectrometer. Chemical shifts were measured relative to the solvent signal and referred to $Si(CH_3)_4$ by an independent measurement.

Results and Discussion

The structure of the compound viewed along the *c* axis is shown in Figure 1. The different purine molecules A and B are shown in Figure 2 with the atom-numbering scheme. Bond distances and angles are listed in Table 2. The structure is centrosymmetric at the all-*trans* $Sn(CH_3)_2Cl_2(H_2O)_2$ octahedral units, which are surrounded by two pairs of purine molecules hydrogen bonded to the H_2O ligands. Each purine also makes hydrogen bonds with purines adjacent to different $Sn(CH_3)_2Cl_2(H_2O)_2$ units to form a three-dimensional network.

The co-ordination bond angles C–Sn–Cl, C–Sn–O, and O–Sn–Cl are close to 90°. The Sn–C and Sn–Cl bond distances are similar to those found for other *trans* octahedral adducts of $Sn(CH_3)_2Cl_2$.[3] The Sn–O bond distance can be compared with the value reported for the anion $[SnCl_5(H_2O)]^-$ (2.24 Å).[4]

The presence of two types of purine molecules, both planar within experimental error, is due to tautomerism of the atom H(13) between atoms N(7) and N(9). In molecules A a hydrogen is attached to atom N(7) of the imidazole ring, as found also in crystals of free purine,[5] whereas in molecules **B** a hydrogen is

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† *Supplementary data available* (No. SUP 56180, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Fractional co-ordinates

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Sn	0.0	0.0	0.0	O	0.093 2(4)	0.106 4(2)	0.078 8(7)
Cl	0.111 9(2)	−0.051 5(1)	0.324 7(2)	$C(CH_3)$	−0.144 9(7)	0.038 6(5)	0.119 4(11)
Molecule A				Molecule B			
N(1)	0.536 2(5)	0.057 4(3)	0.323 5(7)	N(1)	0.002 4(4)	0.235 4(3)	−0.074 5(7)
C(2)	0.420 4(6)	0.057 2(4)	0.229 4(10)	C(2)	0.071 0(6)	0.296 3(4)	−0.058 4(9)
N(3)	0.343 1(4)	0.113 0(3)	0.202 2(7)	N(3)	0.037 1(4)	0.362 0(3)	−0.127 7(7)
C(4)	0.392 4(5)	0.175 5(3)	0.278 3(8)	C(4)	−0.078 3(5)	0.363 2(3)	−0.221 6(8)
C(5)	0.513 3(5)	0.181 3(3)	0.380 1(8)	C(5)	−0.158 4(5)	0.303 6(3)	−0.246 5(8)
C(6)	0.585 2(6)	0.120 9(3)	0.399 4(9)	C(6)	−0.113 0(5)	0.238 7(3)	−0.169 7(8)
N(7)	0.529 0(5)	0.251 9(3)	0.437 9(7)	N(7)	−0.270 5(4)	0.325 4(2)	−0.352 0(7)
C(8)	0.419 8(6)	0.284 6(3)	0.370 2(9)	C(8)	−0.256 6(6)	0.394 3(3)	−0.386 7(9)
N(9)	0.335 3(4)	0.241 3(3)	0.274 9(7)	N(9)	−0.143 9(4)	0.420 2(3)	−0.312 5(7)

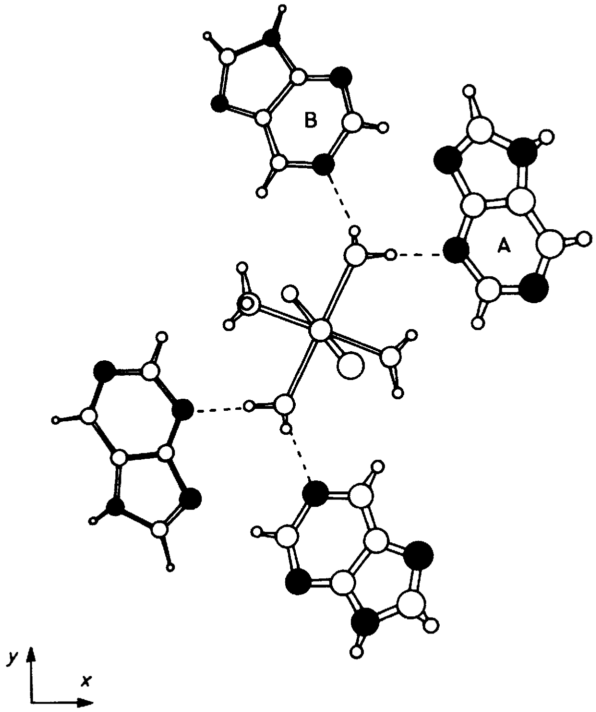
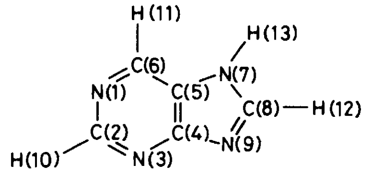
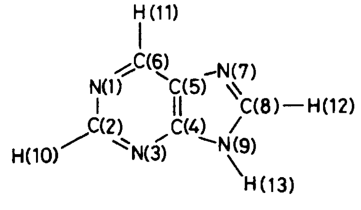


Figure 1. Structure of $Sn(CH_3)_2Cl_2(H_2O)_2{\cdot}4C_5H_4N_4$



Purine A



Purine B

Figure 2. Atom-numbering scheme of purines

attached to N(9). Bond distances and angles of the pyrimidine ring in the two molecules are very close to those reported for free purine; also the C(5)–N(7) and C(4)–N(9) bonds have the same length. The C(8)–N(7) bond is significantly longer than C(8)–N(9) in molecules A, as in free purine, whereas C(8)–N(7) is shorter than C(8)–N(9) in molecules B. Each metal-co-ordinated water molecule is hydrogen bonded to one purine A through N(3) and to one purine B through N(1). Moreover, each purine molecule forms two additional strong hydrogen bonds, *i.e.* N(9)(B)–H ··· N(1)(A) ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $-z$) and N(7)(B)··· H–N(7)(A) ($x - 1, y, z - 1$).

Proton n.m.r. measurements on the system $Sn(CH_3)_2Cl_2$–purine in $(CD_3)_2CO$ show that also in solution direct co-ordination of the base to tin does not occur. The spectrum of purine (0.02 mol dm^{-3}) shows signals at $\delta = 9.1$ [H(11)], 8.9 [H(10)], and 8.5 [H(12)]; NH resonances are not apparent due to exchange with D_2O contained in the solvent. Addition of dimethyltin dichloride in the molar ratio 1 : 1 or 1 : 2 produces no appreciable change in the purine resonances. Similarly, no changes in chemical shift ($\delta = 1.20$) and coupling constants [$J(^{119}Sn-^{1}H) = 86$, $J(^{117}Sn-^{1}H) = 82$ Hz] are observed for the Sn–CH_3 proton resonance upon addition of the base. Measured tin–proton coupling constants for $(CD_3)_2CO$ solutions are considerably greater than J values found for $CDCl_3$ solutions [$J(^{119}Sn-^{1}H) = 69$, $J(^{117}Sn-^{1}H) = 66$ Hz] and are consistent with co-ordination of $Sn(CH_3)_2Cl_2$ with solvent molecules.[6] By addition of D_2O (1 mol dm^{-3}) to a solution of $Sn(CH_3)_2Cl_2$ in $(CD_3)_2CO$ (0.02 mol dm^{-3}) slight changes of the methyl resonances are observed [$\delta = 1.16$; $J(^{119}Sn-^{1}H) = 89$, $J(^{117}Sn-^{1}H) = 85$ Hz]. In the partially aqueous solvent, dimethyltin dichloride is likely to co-ordinate both acetone and water molecules, the interaction with water being increasingly extensive as the solution is evaporated, to give eventually crystals of $Sn(CH_3)_2Cl_2(H_2O)_2{\cdot}4C_5H_4N_4$.

A possible alternative explanation of the structure of the title compound in terms of the $Sn(CH_3)_2Cl_2(OH)_2^{2-}$ anion hydrogen bonded to two purine molecules and two protonated purine cations should be considered. Calculated O–H and N–H bond distances are not sufficiently reliable to allow a distinction between the structures. It is noted, however, that the aqueous $Sn(CH_3)_2^{2+}$ cation, for which values of $pK_{a1} = 3.5$ and $pK_{a2} = 5.5$ are reported,[7] is a weaker acid than protonated purine ($pK_a = 2.4$—2.8).[8] An even lower acid strength should be expected for the uncharged complex $Sn(CH_3)_2Cl_2(H_2O)_2$. Moreover, n.m.r. analysis of the system $Sn(CH_3)_2Cl_2$–purine in $(CD_3)_2CO$–D_2O shows that formation of purine cations does

Table 2. Bond distances (Å) and angles (°)

Co-ordination bonds

Sn–Cl	2.591(1)	O–Sn–O′	180	Cl–Sn–Cl′	180	C–Sn–C′	180
Sn–O	2.235(4)	O–Sn–Cl	88.7(1)	C–Sn–Cl	91.5(2)	C–Sn–O	87.8(3)
Sn–C	2.112(7)	O–Sn–Cl′	91.3(1)	C–Sn–Cl′	88.5(2)	C–Sn–O′	92.2(3)

Purines

	A	B		A	B
N(1)–C(6)	1.354(7)	1.335(7)	N(1)–C(2)	1.335(8)	1.348(8)
N(3)–C(2)	1.332(8)	1.332(8)	N(3)–C(4)	1.341(7)	1.330(7)
C(4)–C(5)	1.406(8)	1.405(7)	C(5)–C(6)	1.362(8)	1.366(8)
N(7)–C(5)	1.362(7)	1.387(7)	N(7)–C(8)	1.361(8)	1.307(8)
N(9)–C(8)	1.317(7)	1.353(7)	N(9)–C(4)	1.365(7)	1.365(7)
C(6)–N(1)–C(2)	118.6(5)	118.8(5)	N(1)–C(2)–N(3)	127.4(6)	127.3(5)
C(2)–N(3)–C(4)	113.5(5)	112.2(5)	N(3)–C(4)–C(5)	123.3(5)	125.5(5)
N(3)–C(4)–N(9)	126.7(5)	128.8(5)	N(9)–C(4)–C(5)	110.0(5)	105.6(5)
C(4)–C(5)–C(6)	118.6(5)	117.0(5)	C(4)–C(5)–N(7)	106.3(5)	109.2(5)
N(7)–C(5)–C(6)	135.1(6)	133.9(5)	N(1)–C(6)–C(5)	118.5(5)	119.2(5)
C(5)–N(7)–C(8)	105.2(5)	104.7(5)	N(7)–C(8)–N(9)	114.6(5)	113.8(5)
C(4)–N(9)–C(8)	104.0(5)	106.7(5)			

Hydrogen bonds

N(3)(A) ··· O	2.762(8)	N(1)(B) ··· O	2.722(8)	N(9)(B) ··· N(1″)(A)	2.805(8)	N(7)B ··· N(7‴)(A)	2.786(8)

Single primes indicate the symmetry-related position $\bar{x}$, $\bar{y}$, $\bar{z}$, double primes $\frac{1}{2} - x$, $\frac{1}{2} + y$, $-\bar{z}$, and triple primes $x - 1$, y, $z - 1$.

not occur to any appreciable extent. The above observations make unlikely a ionic formulation of the reported compound.

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