Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn1	0.35981 (2)	0.28419 (2)	0.61695 (2)	0.06046 (12)
Cl1	0.38740 (8)	0.38490 (6)	0.57433 (8)	0.0994 (4)
C1	0.3657 (2)	0.2333 (2)	0.5305 (2)	0.0548 (9)
C2	0.4041 (2)	0.2074 (2)	0.5349 (2)	0.0592 (10)
C3	0.4066 (3)	0.1709 (2)	0.4814 (3)	0.0760 (14)
C4	0.3707 (3)	0.1599 (3)	0.4233 (3)	0.086 (2)
C5	0.3326 (3)	0.1849 (3)	0.4172 (3)	0.094 (2)
C6	0.3302 (3)	0.2218 (3)	0.4702 (3)	0.0803 (15)
C7	0.4288 (2)	0.3000 (2)	0.6938 (2)	0.0610 (10)
C8	0.4919 (3)	0.3312 (2)	0.6781 (3)	0.087 (2)
C9	0.5361 (3)	0.3395 (3)	0.7280 (4)	0.104 (2)
C10	0.5166 (3)	0.3166 (3)	0.7940 (4)	0.100 (2)
C11	0.4551 (3)	0.2855 (2)	0.8106 (3)	0.0826 (15)
C12	0.4111 (3)	0.2769 (2)	0.7606 (2)	0.0674 (12)
C13	0.2690 (2)	0.2469 (2)	0.6608 (2)	0.0613 (10)
C14	0.2566 (3)	0.2804 (3)	0.7119 (3)	0.0780 (13)
C15	0.1982 (3)	0.2536 (4)	0.7438 (3)	0.093 (2)
C16	0.1525 (3)	0.1940 (4)	0.7256 (3)	0.094 (2)
C17	0.1633 (3)	0.1608 (3)	0.6763 (3)	0.090 (2)
C18	0.2210 (2)	0.1872 (2)	0.6437 (3)	0.0733 (13)
Sn2	2/3	1/3	0.47166 (3)	0.05609 (15)
Cl2	2/3	1/3	0.59582 (11)	0.0913 (7)
C19	0.6239 (2)	0.2369 (2)	0.4450 (2)	0.0534 (9)
C20	0.5680 (2)	0.2074 (2)	0.4074 (2)	0.0647 (11)
C21	0.5391 (2)	0.1441 (2)	0.3919 (3)	0.0751 (13)
C22	0.5659 (3)	0.1096 (2)	0.4138 (3)	0.0804 (14)
C23	0.6214 (3)	0.1380 (3)	0.4502 (3)	0.083 (2)
C24	0.6504 (2)	0.2012 (2)	0.4658 (2)	0.0685 (12)

Table 2. *Selected geometric parameters* (Å, °)

Sn1—C13	2.109 (4)	Sn1—Cl1	2.3535 (12)
Sn1—C1	2.118 (4)	Sn2—C19	2.112 (4)
Sn1—C7	2.124 (4)	Sn2—Cl2	2.374 (2)
C13—Sn1—C1	115.0 (2)	C8—C7—Sn1	121.4 (3)
C13—Sn1—C7	112.0 (2)	C12—C7—Sn1	120.6 (3)
C1—Sn1—C7	111.5 (2)	C18—C13—C14	117.6 (4)
C13—Sn1—Cl1	106.22 (12)	C18—C13—Sn1	121.3 (3)
C1—Sn1—Cl1	106.13 (11)	C14—C13—Sn1	120.9 (4)
C7—Sn1—Cl1	105.27 (11)	C19—Sn2—C19^i	114.36 (8)
C2—C1—C6	117.4 (4)	C19—Sn2—Cl2	103.97 (10)
C2—C1—Sn1	119.1 (3)	C24—C19—C20	118.2 (4)
C6—C1—Sn1	123.3 (3)	C24—C19—Sn2	120.7 (3)
C8—C7—C12	117.9 (4)	C20—C19—Sn2	121.1 (3)

Symmetry code: (i) $1 - y, x - y, z$.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(cytosinium) Tetrachlorodimethyl-stannate(IV)

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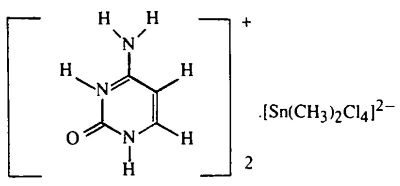
Abstract

The structure of the title compound, bis(4-amino-2-oxo-1,2-dihydropyrimidinium) tetrachlorodimethyl-stannate(IV), $(C_4H_6N_3O)_2[SnCl_4(CH_3)_2]$, consists of discrete $C_4H_6N_3O^+$ (cytosinium) cations and $[SnCl_4(CH_3)_2]^{2-}$ anions in which the Sn atom is six-coordinate *trans*-octahedral. The crystal packing of the ionic complex is stabilized by intermolecular N—H···Cl bonds between the anions and neighbouring cytosinium cations.

Comment

The antitumor activity of organotin(IV) complexes is known (Kabanos, Keramidas, Mentzafos, Russo, Terzis & Tsangaris, 1992). Because of interest in the possible interaction of these compounds with the constituents of nucleic acids, we report here the crystal structure of the title compound, $(C_4H_6N_3O)_2[SnCl_4(CH_3)_2]$, (I).



(I)

The title structure (Fig. 1) consists of discrete $C_4H_6N_3O^+$ and $[SnCl_4(CH_3)_2]^{2-}$ ions held together by a network of N—H···Cl hydrogen bonds. The $[SnCl_4(CH_3)_2]^{2-}$ anion is octahedral with the metal atom located in a special position on a crystallographic inversion centre. The cytosinium ring is involved in a rather complicated hydrogen-bonding network with the anion. As shown in Table 3, each coordinated Cl(1) atom is involved in bifurcated hydrogen bonds with the H—N(3) and H—N(4)H groups of the same cation, and the Cl(2) atom forms hydrogen bonds with the H—N(1) and H—N(4)H groups of two different cations, so that each centrosymmetric $[SnCl_4(CH_3)_2]^{2-}$ anion is hydrogen bonded to six cations, which gives a compactness and stability to the crystal packing.

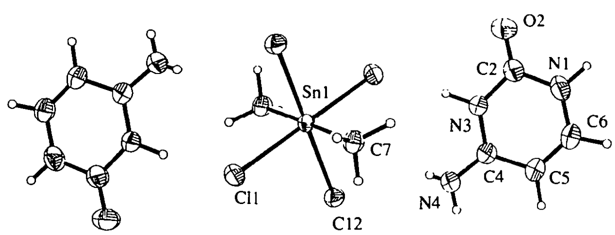


Fig. 1. The crystal structure of $(C_4H_6N_3O)_2[SnCl_4(CH_3)_2]$ shown with 50% probability displacement ellipsoids.

Coordination bond lengths are similar to those found in other octahedral Sn^{IV} compounds. In particular, the Sn—Cl distances of 2.620 (1) and 2.649 (1) Å compare well with values of 2.603 (2) and 2.625 (2) Å in $(py)_2[(CH_3)_2SnCl_4]$ (py = pyridinium) (Smart & Webster, 1976), 2.6047 (5) and 2.6189 (5) Å in $(aca)_2[(CH_3)_2SnCl_4].2H_2O$ [aca = 2-(aminocarbonyl)anilinium] (Nasser, Hossein, van der Helm & Zuckerman, 1984), 2.599 (5) and 2.600 (3) Å in $(ttf)_3[(CH_3)_2SnCl_4]$ (ttf = tetrathiafulvalenium) (Matsubayashi, Ueyama & Tanaka, 1985), and 2.627 (1) and 2.628 (1) Å in $(ap)_2[(CH_3)_2SnCl_4]$ (ap = 2-aminopyridinium) (Valle, Sánchez-Gonzáles, Ettorre & Plazzogna, 1988). The observed differences in the Sn—Cl bond lengths can be ascribed mainly to hydrogen-bonding effects causing elongation of these bonds. Thus, the shortest Sn—Cl distances are found for the tetrathiafulvalenium compound in which no hydrogen bonds are present; the difference in the average Sn—Cl distances between this and the cytosinium compound is 0.035 Å.

Comparison of the structural details of the cytosinium cation with those of the cytosine molecule itself (McClure & Craven, 1973) shows that protonation produces an increase of about 0.02 Å in the N(3)—C(2) and N(3)—C(4) distances, a decrease of 0.03 Å in the C(4)—N(4) distance, an increase of 5.6° in the C(2)—N(3)—C(4) angle and a decrease of about 4.5° in the N(3)—C(4)—C(5) and N(3)—C(2)—N(1) angles. A similar effect has been observed in the structure of cytosinium dihydrogenmonophosphate (Bagieu-Beucher, 1990).

Experimental

Crystals of the title compound were prepared by slow evaporation of a 2:1 mixture of cytosine and dichlorodimethyltin in concentrated hydrochloric acid.

Crystal data

$(C_4H_6N_3O)_2[SnCl_4(CH_3)_2]$	Mo $K\alpha$ radiation
$M_r = 514.8$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	$\theta = 6–12°$
$a = 6.967$ (1) Å	$\mu = 1.982$ mm^{-1}
$b = 10.346$ (2) Å	$T = 293$ K
$c = 12.877$ (3) Å	Prism
$\beta = 94.12$ (3)°	0.4 × 0.3 × 0.3 mm
$V = 926$ (1) Å^3	White
$Z = 2$	
$D_x = 1.84$ Mg m^{-3}	

Data collection

Philips PW1100 diffractometer	$R_{int} = 0.069$
θ–2θ scans	$\theta_{max} = 28°$
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)	$h = -9 \rightarrow 9$
$T_{min} = 0.82$, $T_{max} = 1.00$	$k = -2 \rightarrow 13$
2095 measured reflections	$l = 0 \rightarrow 16$
1981 independent reflections	2 standard reflections monitored every 100 reflections
1913 observed reflections [$F > 3\sigma(F)$]	intensity decay: none

Refinement

Refinement on F	Unit weights applied
$R = 0.028$	$(\Delta/\sigma)_{max} = 0.1$
$wR = 0.028$	$\Delta\rho_{max} = 1.0$ e Å^{-3}
$S = 1.024$	$\Delta\rho_{min} = 0.6$ e Å^{-3}
1913 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
121 parameters	
Only coordinates of H atoms refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn(1)	0	1/2	1/2	0.02905 (9)
Cl(1)	0.0992 (1)	0.30107 (9)	0.62180 (8)	0.0426 (3)
Cl(2)	0.2779 (1)	0.44628 (9)	0.38024 (8)	0.0391 (3)

C(5)	0.5419 (6)	0.9725 (4)	0.3670 (3)	0.038 (1)
C(4)	0.3979 (5)	0.8776 (3)	0.3725 (3)	0.035 (1)
N(4)	0.4349 (5)	0.7532 (3)	0.3713 (3)	0.048 (1)
N(3)	0.2142 (4)	0.9172 (3)	0.3819 (2)	0.0359 (9)
C(2)	0.1536 (6)	1.0447 (4)	0.3793 (3)	0.042 (1)
O(2)	−0.0135 (4)	1.0739 (3)	0.3816 (3)	0.064 (1)
N(1)	0.3001 (5)	1.1321 (3)	0.3729 (3)	0.046 (1)
C(6)	0.4882 (6)	1.0958 (4)	0.3662 (3)	0.041 (1)
C(7)	0.1891 (5)	0.6170 (4)	0.5943 (3)	0.039 (1)

Table 2. *Selected geometric parameters* (Å, °)

Sn(1)—Cl(1)	2.649 (1)	Sn(1)—Cl(2)	2.620 (1)
Sn(1)—C(7)	2.109 (4)	N(1)—C(2)	1.371 (5)
N(1)—C(6)	1.372 (5)	N(3)—C(2)	1.384 (5)
C(2)—O(2)	1.205 (5)	N(3)—C(4)	1.358 (5)
C(4)—C(5)	1.409 (5)	N(4)—C(4)	1.313 (6)
C(5)—C(6)	1.329 (6)		
Cl(1)—Sn(1)—Cl(2)	90.64 (4)	C(2)—N(3)—C(4)	125.0 (3)
C(7)—Sn(1)—Cl(1)	88.8 (1)	N(3)—C(4)—C(5)	118.3 (3)
C(7)—Sn(1)—Cl(2)	90.2 (1)	N(3)—C(4)—N(4)	119.0 (3)
C(2)—N(1)—C(6)	122.8 (3)	N(4)—C(4)—C(5)	122.8 (4)
N(1)—C(2)—N(3)	113.8 (3)	C(4)—C(5)—C(6)	117.9 (4)
N(1)—C(2)—O(2)	124.1 (4)	C(5)—C(6)—N(1)	122.1 (4)
N(3)—C(2)—O(2)	122.3 (4)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(3)—H(3)···Cl(1^{i})	0.97 (5)	2.18 (5)	3.139 (3)	169 (5)
N(4)—H(42)···Cl(1^{ii})	0.75 (6)	2.55 (6)	3.289 (4)	168 (5)
N(1)—H(1)···Cl(2^{iii})	0.94 (6)	2.34 (6)	3.256 (4)	165 (4)
N(4)—H(41)···Cl(2)	0.82 (6)	2.65 (6)	3.363 (4)	145 (5)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, 1+y, z$.

The structure was solved by the heavy-atom method and final scale factors, atomic coordinates and anisotropic displacement parameters were obtained by full-matrix least-squares refinement. H-atom positions were obtained from the electron density map and refined with a fixed displacement parameter (U_{iso} = 0.08 Å^2). All calculations were performed on a MicroVAX computer using *SHELX*76 (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including intermolecular distances, have been deposited with the IUCr (Reference: NA1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaquabis(dichloroacetato)bis(1,10-phenanthroline)europium(III) Dichloroacetate and the Corresponding Erbium(III) Complex

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Abstract

The title complexes, diaquabis(dichloroacetato)bis(1,10-phenanthroline)europium(III) dichloroacetate, $[Eu(CHCl_2CO_2)_2(C_{12}H_8N_2)_2(H_2O)_2]CHCl_2CO_2$, and diaquabis(dichloroacetato)bis(1,10-phenanthroline)erbium(III) dichloroacetate, $[Er(CHCl_2CO_2)_2(C_{12}H_8N_2)_2(H_2O)_2]CHCl_2CO_2$, are isostructural. The central atom in each is eight-coordinate and the coordination polyhedra are slightly distorted square antiprisms. The phenanthroline and dichloroacetato ligands compete to coordinate to the lanthanide ions. The structures of the series of lanthanide complexes Ln = La to Yb fall into two types, changing structure between Sm and Eu.

Comment

Since the discovery of the lanthanide elements, the coordination chemistry of the trivalent lanthanide(III) ions has received considerable attention (Moeller, 1963; Choppin, 1989). Trivalent *f*-block ions are oxophilic and prefer to form coordination complexes with anionic or neutral ligands that have strong O and N-atom donor centres. The design of ligands capable of forming stable lanthanide(III) complexes would allow further study of the coordination properties of these ions. However, there are relatively few reports of lanthanide(III) complexes with heterocyclic amine bidentate ligands. Having completed our research on the complexes of lanthanide trichloroacetate with one bidentate heterocyclic amine ligand (Huang, Lu & Dong, 1990; Dong, Hong, Barton & Robertson, 1990; Mao, Lu & Dong, 1989), we studied the synthesis of the series of complexes of lanthanide(III) trichloroacetate or dichloroacetate (dea) with two bidentate heterocyclic amine