ω–2θ scans

Absorption correction:
empirical σ scans (North *et al.*, 1968)
$T_{min} = 0.745$, $T_{max} = 0.838$
1800 measured reflections
1663 independent reflections

$R_{int} = 0.012$
$\theta_{max} = 27.49°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -8 \rightarrow 7$
3 standard reflections
every 150 reflections
intensity decay: 0.12%

Refinement

Refinement on F
$R = 0.029$
$wR = 0.039$
$S = 1.122$
1555 reflections
89 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o)$
$+ 0.00063|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.049$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—N1	2.071 (2)	N1—C1	1.472 (3)
Ni1—N2	2.154 (2)	N2—C2	1.467 (3)
Ni1—N3	2.151 (2)	N2—C3	1.473 (4)
O1—N3	1.237 (3)	C1—C2	1.514 (4)
O2—N3	1.239 (3)	C3—C4	1.513 (4)
N1—Ni1—N2	82.84 (8)	N2—Ni1—N3^i	89.99 (7)
N1—Ni1—N3	91.16 (8)	N1—C1—C2	109.3 (2)
N1—Ni1—N2^i	97.16 (8)	N2—C2—C1	108.99 (17)
N1—Ni1—N3^i	88.84 (8)	N2—C3—C4	115.5 (2)
N2—Ni1—N3	90.01 (7)		

Symmetry code: (i) $2 - x, -y, 2 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots$A	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A
N1—H1$\cdots$O2^i	0.95	2.29	2.920 (3)	123
N1—H2$\cdots$O1^{iii}	0.95	2.30	3.104 (3)	142
N2—H3$\cdots$O1^{iii}	0.95	2.48	3.340 (2)	150
N2—H3$\cdots$O2^{iii}	0.95	2.24	3.118 (3)	154

Symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $1 - x, -y, 2 - z$; (iii) $2 - x, -y, 3 - z$.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1997). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1998).

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Bis(guanidinium) hexachlorostannate(IV)

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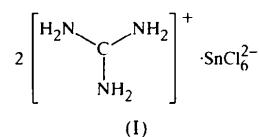
Abstract

The title complex, $(CH_6N_3)_2[SnCl_6]$, consists of planar $[C(NH_2)_3]^+$ ions and a slightly distorted $[SnCl_6]^{2-}$ octahedron connected by weak N—H$\cdots$Cl hydrogen bonds, forming parallel sheets in the crystal.

Comment

The molecular motion of the guanidinium ion in $(CH_6N_3)_2[SnCl_6]$, (I), was studied by solid-state ^{1}H NMR (Furukawa & Nakamura, 1986). The 120° reorientational jumps of the cation about its C_3 axis were found to occur above room temperature. The activation energy for this motion is 52 kJ mol^{-1}, which is much larger than those of 4.2–10.0 kJ mol^{-1} for the reorientational motions accompanied by breaking the N—H$\cdots$Cl hydrogen bonds in A_2SnCl_6 complexes [A = NH_4, CH_3NH_3 and $(CH_3)_3CNH_3$; Strange & Terenzi, 1972; Ikeda *et al.*, 1976; Ishida *et al.*, 1992].

(I)

The structure of the title complex consists of planar [C(NH₂)₃]⁺ and distorted octahedral [SnCl₆]²⁻ ions forming sheets parallel to the *ab* plane (Fig. 1). The [SnCl₆]²⁻ octahedron is noncentrosymmetric but has a twofold symmetry. The bond length and angles in both the anion and cation are normal. This complex shows three ^{35}Cl nuclear quadrupole resonance (NQR) frequencies (ν_1 = 16.513, ν_2 = 16.215 and ν_3 = 15.980 MHz) at room temperature, consistent with the crystal structure. The temperature dependence of the resonance frequencies shows no phase transition from 77 to 370 K. In the sheet, the cation and anion are held together by N—H···Cl hydrogen bonds in such a way that each cation is hydrogen bonded to three anions and
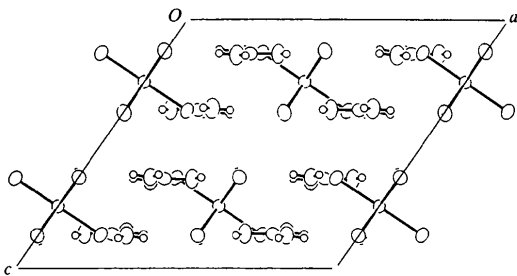

Fig 1. Packing diagram viewed down the *b* axis. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size.
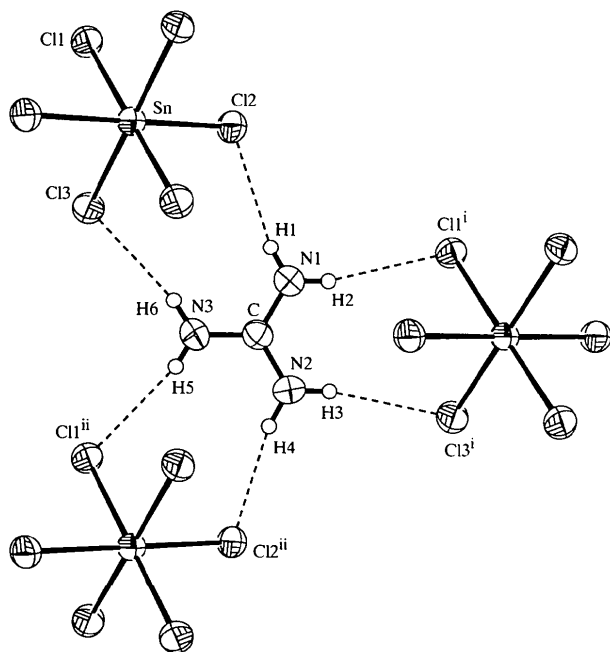

Fig 2. *ORTEP*-3 (Farrugia, 1997) view of (I) showing the atomic numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $\frac{1}{2}+x$, $\frac{1}{2}+y$, z; (ii) x, $1+y$, z.]

each Cl atom of the anion is the recipient of hydrogen bonds from two H atoms (Fig. 2).

The H···Cl and N···Cl distances are 2.56–2.66 and 3.413–3.456 Å, respectively (Table 2), which are comparable to those of 2.61–2.89 and 3.30–3.60 Å found in weak bifurcated or trifurcated N—H···Cl bonds in A_2SnCl₆ [A = NH₄, CH₃NH₃, (CH₃)₂NH₂, (CH₃)₃NH, C₂H₅NH₃, (C₃H₇)₃NH; Knop *et al.*, 1979, 1983; Kitahama *et al.*, 1979], implying that the hydrogen bonds in the present complex are weak. The hydrogen bonds are, therefore, considered to have a negligible effect on the hindering barrier of the cation reorientation. When the cation rotates about its pseudo-C_3 axis in the crystal, the shortest N···Cl contact distance between the cation and anion is calculated to be 3.1 Å, which is shorter than the sum of van der Waals radii (3.3 Å) of Cl and N atoms. Thus, the steric repulsion between the N and Cl atoms is considered to be the origin of the hindering barrier for the motion.

Experimental

Crystals of the title complex were grown by slow evaporation from a concentrated HCl solution containing stoichiometric amounts of C(NH₂)₃Cl and SnCl₄.

Crystal data

(CH₆N₃)₂[SnCl₆]	Mo $K\alpha$ radiation
M_r = 451.57	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
a = 15.144 (3) Å	θ = 11.8–12.5°
b = 8.672 (1) Å	μ = 2.69 mm⁻¹
c = 14.230 (3) Å	T = 298 K
β = 124.79 (1)°	Prismatic
V = 1534.7 (5) Å³	0.15 × 0.15 × 0.12 mm
Z = 4	Colourless
D_x = 1.954 Mg m⁻³	
D_m = 1.95 (1) Mg m⁻³	

Data collection

Rigaku AFC-5R diffractometer	1253 reflections with $I > 2\sigma(I)$
ω–2θ scans	R_{int} = 0.014
Absorption correction:	θ_{max} = 27.48°
ψ scans (North *et al.*, 1968)	h = 0 → 19
	k = 0 → 11
T_{min} = 0.67, T_{max} = 0.72	l = −18 → 15
1952 measured reflections	3 standard reflections
1763 independent reflections	every 100 reflections
	intensity decay: 2.2%

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.96 e Å⁻³
$R(F)$ = 0.032	$\Delta\rho_{min}$ = −0.85 e Å⁻³
$wR(F^2)$ = 0.036	Extinction correction:
S = 1.23	Zachariasen (1967)
1763 reflections	Extinction coefficient:
94 parameters	1.95 (9) × 10⁻⁷

All H atoms refined
$w = 1/[\sigma^2(F_o)$
$\quad + 0.00001|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.01$

Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn—Cl1	2.436 (1)	N1—C	1.314 (5)
Sn—Cl2	2.429 (1)	N2—C	1.316 (5)
Sn—Cl3	2.422 (1)	N3—C	1.312 (4)
Cl1—Sn—Cl1^i	88.35 (5)	Cl2—Sn—Cl3	89.90 (4)
Cl1—Sn—Cl2	91.05 (3)	Cl2—Sn—Cl3^i	90.21 (4)
Cl1—Sn—Cl2^i	88.84 (3)	Cl3—Sn—Cl3^i	91.24 (6)
Cl1—Sn Cl3	90.21 (3)	N1 C- N2	120.3 (3)
Cl1—Sn—Cl3^i	178.07 (4)	N1—C—N3	120.0 (4)
Cl2—Sn—Cl2^i	179.84 (6)	N2—C—N3	119.7 (4)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯Cl2	0.81 (3)	2.63 (4)	3.414 (4)	164 (4)
N1—H2⋯Cl1^i	0.83 (3)	2.63 (3)	3.429 (4)	162 (3)
N2—H3⋯Cl3^i	0.84 (4)	2.63 (4)	3.456 (4)	170 (4)
N2—H4⋯Cl2^{ii}	0.87 (3)	2.56 (4)	3.413 (4)	168 (4)
N3—H5⋯Cl1^{ii}	0.77 (3)	2.66 (3)	3.421 (4)	166 (3)
N3—H6⋯Cl3	0.84 (4)	2.62 (4)	3.439 (4)	167 (3)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $x, 1 + y, z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN for Windows*. Software used to prepare material for publication: *TEXSAN for Windows*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1486). Services for accessing these data are described at the back of the journal.

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Diaquabis(hydrogen phthalato)copper(II), a new phase

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Abstract

In the title compound, β-[Cu(C$_8$H$_5$O$_4$)$_2$(H$_2$O)$_2$]$_n$, the Cu atom lies on an inversion centre and has a tetragonal distortion from octahedral symmetry. Each hydrogen phthalate ligand is coordinated to two metals, forming a polymeric structure. The aromatic ring and the carboxylate group form an approximate plane, with the carboxylic acid group plane almost perpendicular to it. An intermolecular hydrogen bond between hydrogen phthalate groups is observed, with an O⋯O distance of 2.614 (2) Å.

Comment

The structure of α-[Cu(C$_8$H$_5$O$_4$)$_2$(H$_2$O)$_2$], (II), has been reported by Goeta *et al.* (1993), Bartl & Küppers (1980) (neutron data), Cingi *et al.* (1969) and Cingi & Magnano (1959). In that phase, as well as in structures such as [Co(C$_8$H$_5$O$_4$)$_2$]·6H$_2$O (Küppers, 1990), [Mg(H$_2$O)$_6$](C$_8$H$_5$O$_4$)$_2$·2H$_2$O (Kariuki & Jones, 1989), [Li(C$_8$H$_5$O$_4$)]·H$_2$O (Küppers *et al.*, 1985) and [Li(C$_8$H$_5$O$_4$)]·CH$_3$OH (Küppers *et al.*, 1981), the ligand shows a planar configuration, having a short intramolecular hydrogen bond between the two carboxylate groups, with O⋯O distances of around 2.4 Å. On the other hand, crystals of K(C$_8$H$_5$O$_4$)·0.5H$_2$O (Kariuki & Jones, 1995), [Co(H$_2$O)$_6$](C$_8$H$_5$O$_4$)$_2$ (Kariuki & Jones, 1993) and [N(CH$_3$)$_4$](C$_8$H$_5$O$_4$) (Jessen, 1990) do exhibit an intermolecular hydrogen bond once the carboxylate and carboxylic acid groups form two planes approximately perpendicular to each other. The structure reported here, β-[Cu(C$_8$H$_5$O$_4$)$_2$(H$_2$O)$_2$]$_n$, (I), belongs to the latter