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# Bis(dicyclohexylammonium) Aquadimethyldi(oxalato-*O*,*O'*)stannate Ethanol Solvate

Seik Weng Ng

*Institute of Advanced Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: hlnswen@cc.um.edu.my*

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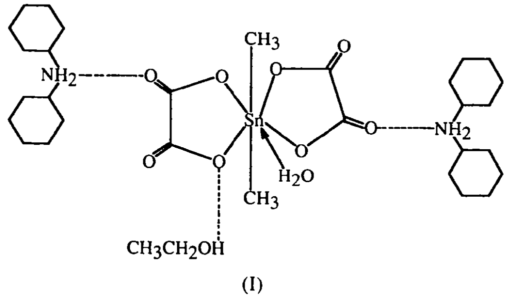
## Abstract

The Sn atom in the title compound, $[(C_6H_{11})_2NH_2]_2[Sn(C_2O_4)_2(CH_3)_2(H_2O)].C_2H_6O$, is chelated by two isobidentate oxalato groups and exists in a *trans*-$C_2SnO_5$ pentagonal-bipyramidal environment [C—Sn—C 173.5 (2)°]. The coordinated water molecule is hydrogen bonded to a carbonyl O atom of an adjacent stannate [O···O 2.796 (3) Å] to form a centrosymmetric dinuclear tetraanion. These are linked into sheets through the two ammonium cations [N···O 2.783 (3), 2.790 (3), 2.793 (3) and 2.848 (3) Å]. The ethanol solvate molecule is hydrogen bonded to another doubly-bonded carbonyl O atom [O···O 2.819 (9) Å].

## Comment

Dialkyltin bis-chelates generally adopt a skew-trapezoidal bipyramidal geometry (C—Sn—C 135–155°) if the chelating group has a small bite (Ng, Chen, Kumar Das & Mak, 1987). The present compound was anticipated to have a structure similar to that of bis(dicyclohexylammonium) dibutyldioxalatostannate (Ng, Kumar Das, Gielen & Tiekink, 1992), but its synthesis in the same solvent (ethanol) yielded the stannate as a water-coordinated ethanol solvate. The expansion in coordination number of tin in $[R_2Sn(O_2CCO_2)_2]^{2-}$, from six in the $R = C_4H_9$ derivative to seven in the $R = CH_3$ derivative, is accompanied by a linearization of the $R_2Sn$ skeleton [from 146.7 (3) to 175.2 (2)°]. A similar widening of the C—Sn—C angle has been found in the dimethyltin diacetate/dimethyltriacetatostannate system [135.9 (2) and 165.8 (6)°] (Lockhart, Calabrese & Davidson, 1987).



(I)

Two aquadimethyldioxalatostannate ethanol solvate units are linked across a centre of inversion, by a hydrogen bond involving the water molecule, to give a dinuclear entity; these entities are further linked into sheets by hydrogen bonds through the dicyclohexylammonium counter ions. The fact that the sheets are relatively porous probably explains the inclusion of ethanol in the crystal structure. The Sn←$O_{water}$ bond distance is similar to distances found in organotin hydrates (Ng, 1996; Ng & Kumar Das, 1995).

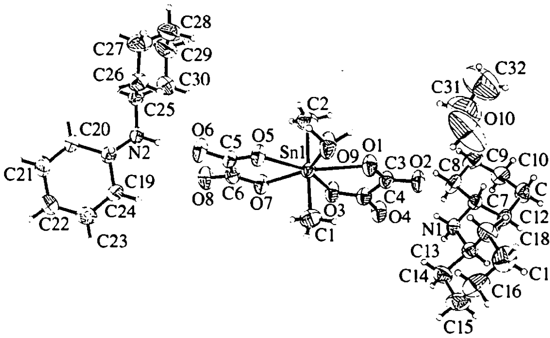


Fig. 1. *ORTEP* (Sheldrick, 1990) plot of bis(dicyclohexylammonium) aquadimethyldioxalatostannate ethanol solvate at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

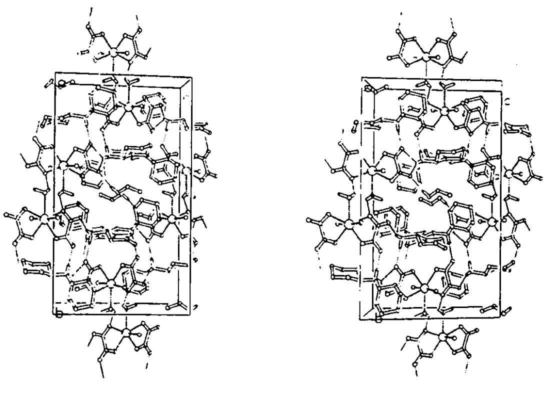


Fig. 2. *PLUTON* (Spek, 1994) plot showing the hydrogen-bonding interactions.

## Experimental

The title ethanol solvate was the unexpected compound obtained when dicyclohexylamine, dimethyltin oxide and oxalic acid dihydrate (molar ratio 2:1:2) were reacted in ethanol. The amine and the acid were heated in a small volume of ethanol and the oxide was added to the solution. The mixture was heated until the oxide dissolved completely. Slow cooling of the filtered solution yielded large crystals of the ammonium stannate.

### Crystal data

$(C_{12}H_{24}N)_2[Sn(C_2O_4)_2(CH_3)_2(H_2O)].C_2H_6O$
$M_r = 753.53$
Monoclinic
$P2_1/n$
$a = 12.815 (1)$ Å
$b = 22.5637 (8)$ Å
$c = 13.224 (1)$ Å
$\beta = 101.306 (4)°$
$V = 3749.4 (5)$ Å$^3$
$Z = 4$
$D_x = 1.335$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–13°$
$\mu = 0.734$ mm$^{-1}$
$T = 298 (2)$ K
Block
0.55 × 0.55 × 0.55 mm
Colourless

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.61$, $T_{\max} = 0.67$
7901 measured reflections
7558 independent reflections

6025 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0212$
$\theta_{\max} = 26.22°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 28$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: 1.9%

### Refinement

Refinement on $F^2$
$R(F) = 0.0345$
$wR(F^2) = 0.0883$
$S = 1.027$
7558 reflections
406 parameters
H atoms: $U(\rm H) = 1.5U_{\rm eq}(\rm C,N,O)$; water H atoms were placed at calculated positions

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.7754P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.652$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.680$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Sn1 | 0.87831 (1) | 0.38875 (1) | 0.06569 (1) | 0.03392 (7) |
| O1 | 0.8122 (2) | 0.4289 (1) | 0.2019 (2) | 0.0560 (6) |
| O2 | 0.7232 (2) | 0.4072 (1) | 0.3253 (2) | 0.0597 (6) |
| O3 | 0.8199 (2) | 0.3150 (1) | 0.1527 (2) | 0.0499 (5) |
| O4 | 0.7165 (2) | 0.2927 (1) | 0.2639 (2) | 0.0559 (6) |
| O5 | 0.9551 (2) | 0.4218 (1) | −0.0673 (2) | 0.0498 (5) |
| O6 | 1.0419 (2) | 0.3941 (1) | −0.1883 (2) | 0.0591 (6) |
| O7 | 0.9200 (2) | 0.3099 (1) | −0.0223 (2) | 0.0471 (5) |
| O8 | 1.0126 (2) | 0.2793 (1) | −0.1391 (2) | 0.0584 (6) |
| O9 | 0.8808 (2) | 0.4963 (1) | 0.0652 (2) | 0.0770 (8) |
| O10 | 0.7850 (5) | 0.4969 (2) | 0.4731 (3) | 0.202 (3) |
| N1 | 0.5697 (2) | 0.3389 (1) | 0.4036 (2) | 0.0370 (5) |
| N2 | 1.1857 (2) | 0.3282 (1) | −0.2750 (2) | 0.0378 (5) |
| C1 | 0.7278 (3) | 0.3979 (2) | −0.0289 (3) | 0.0643 (9) |
| C2 | 1.0303 (3) | 0.3899 (2) | 0.1585 (3) | 0.075 (1) |
| C3 | 0.7668 (2) | 0.3940 (1) | 0.2532 (2) | 0.0426 (6) |
| C4 | 0.7670 (2) | 0.3279 (1) | 0.2210 (2) | 0.0414 (6) |
| C5 | 0.9919 (2) | 0.3834 (1) | −0.1202 (2) | 0.0398 (6) |
| C6 | 0.9733 (2) | 0.3178 (1) | −0.0923 (2) | 0.0390 (6) |
| C7 | 0.6201 (2) | 0.3443 (1) | 0.5154 (2) | 0.0375 (6) |
| C8 | 0.7161 (2) | 0.3035 (2) | 0.5354 (2) | 0.0553 (8) |
| C9 | 0.7707 (2) | 0.3044 (2) | 0.6490 (3) | 0.0645 (9) |
| C10 | 0.6938 (3) | 0.2892 (2) | 0.7173 (2) | 0.0594 (8) |
| C11 | 0.5983 (3) | 0.3298 (2) | 0.6974 (2) | 0.0614 (9) |
| C12 | 0.5421 (2) | 0.3292 (1) | 0.5849 (2) | 0.0467 (7) |
| C13 | 0.4704 (2) | 0.3736 (1) | 0.3641 (2) | 0.0414 (6) |
| C14 | 0.4339 (3) | 0.3595 (2) | 0.2505 (2) | 0.0563 (8) |
| C15 | 0.3302 (3) | 0.3925 (2) | 0.2074 (3) | 0.073 (1) |
| C16 | 0.3442 (3) | 0.4581 (2) | 0.2240 (3) | 0.083 (1) |
| C17 | 0.3832 (3) | 0.4724 (2) | 0.3367 (3) | 0.084 (1) |
| C18 | 0.4866 (3) | 0.4394 (1) | 0.3815 (3) | 0.0595 (9) |
| C19 | 1.1459 (2) | 0.3383 (1) | −0.3882 (2) | 0.0398 (6) |
| C20 | 1.2271 (2) | 0.3194 (1) | −0.4514 (2) | 0.0456 (7) |
| C21 | 1.1813 (3) | 0.3228 (2) | −0.5661 (2) | 0.0594 (9) |
| C22 | 1.0785 (3) | 0.2878 (2) | −0.5946 (3) | 0.0633 (9) |
| C23 | 0.9980 (3) | 0.3092 (2) | −0.5332 (3) | 0.068 (1) |
| C24 | 1.0420 (2) | 0.3042 (2) | −0.4183 (2) | 0.0582 (8) |
| C25 | 1.2893 (2) | 0.3557 (1) | −0.2257 (2) | 0.0406 (6) |
| C26 | 1.2895 (3) | 0.4226 (1) | −0.2413 (3) | 0.0531 (8) |
| C27 | 1.3936 (3) | 0.4494 (2) | −0.1835 (3) | 0.070 (1) |
| C28 | 1.4173 (3) | 0.4325 (2) | −0.0709 (3) | 0.075 (1) |
| C29 | 1.4180 (3) | 0.3657 (2) | −0.0579 (3) | 0.069 (1) |
| C30 | 1.3116 (3) | 0.3396 (1) | −0.1121 (2) | 0.0556 (8) |
| C31 | 0.8657 (6) | 0.4700 (4) | 0.5409 (7) | 0.191 (4) |
| C32 | 0.9248 (7) | 0.4906 (4) | 0.6291 (5) | 0.210 (4) |

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

| | | | |
|---|---|---|---|
| Sn1—C1 | 2.093 (3) | Sn1—O5 | 2.301 (2) |
| Sn1—C2 | 2.088 (3) | Sn1—O7 | 2.247 (2) |
| Sn1—O1 | 2.319 (2) | Sn1—O9 | 2.428 (2) |
| Sn1—O3 | 2.235 (2) | | |
| C1—Sn1—C2 | 173.5 (2) | O1—Sn1—O3 | 71.40 (6) |
| C1—Sn1—O1 | 89.5 (1) | O1—Sn1—O5 | 137.99 (7) |
| C1—Sn1—O3 | 91.1 (1) | O1—Sn1—O7 | 150.61 (7) |
| C1—Sn1—O5 | 89.6 (1) | O1—Sn1—O9 | 67.58 (7) |
| C1—Sn1—O7 | 93.1 (1) | O3—Sn1—O5 | 150.61 (7) |
| C1—Sn1—O9 | 84.9 (1) | O3—Sn1—O7 | 79.28 (7) |
| C2—Sn1—O1 | 88.8 (1) | O3—Sn1—O9 | 138.79 (7) |
| C2—Sn1—O3 | 94.3 (1) | O5—Sn1—O7 | 71.34 (6) |
| C2—Sn1—O5 | 87.5 (1) | O5—Sn1—O9 | 70.52 (6) |
| C2—Sn1—O7 | 91.4 (1) | O7—Sn1—O9 | 141.81 (7) |
| C2—Sn1—O9 | 88.7 (1) | | |

Table 3. *Contact distances (Å)*

| | | | |
|---|---|---|---|
| N1···O2 | 2.848 (3) | N2···O6 | 2.783 (3) |
| N1···O8$^{\rm i}$ | 2.793 (3) | O2···O10 | 2.819 (9) |
| N2···O4$^{\rm ii}$ | 2.790 (3) | O9···O5$^{\rm iii}$ | 2.796 (3) |

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

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990) and *PLUTON* (Spek, 1994). 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: SK1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Solvate-Dependent Polymorphism: Crystallization of $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$ from $CH_2Cl_2$ as a Mono-Solvate in the Rare Tetragonal Space Group *P*4$_2$*/mbc*

TRACY L. UTZ, STEVEN J. GEIB AND N. JOHN COOPER

*Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA. E-mail: geib+@pitt.edu*

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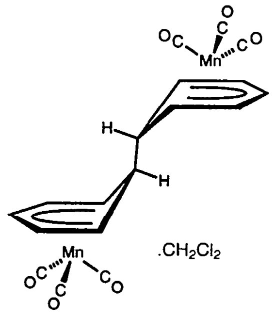
## Abstract

Recrystallization from methylene chloride gives a tetragonal pseudo-polymorph of ($\mu$-$\eta^5$:$\eta^5$-bicyclohexadienyl)bis(tricarbonylmanganese), $[Mn_2(C_{12}H_{12})(CO)_6].CH_2Cl_2$, in the rare space group *P*4$_2$*/mbc*. Molecules in these crystals and in the monoclinic unsolvated form are virtually superimposable, and it is the inclusion of the methylene chloride solvate molecule which allows for crystallization in *P*4$_2$*/mbc*. The Mn dimers are packed in layers with fourfold symmetry, with disordered methylene chloride molecules filling interstices between the layers.

## Comment

There is considerable current interest in the controlled engineering of crystals using the forces commonly found in the crystalline environment which determine crystal-packing arrangements (Desiraju, 1989). Insight into such forces can be obtained from studies of systems in which changes in crystallization conditions such as temperature, solvent, counterion and concentration, cause a given compound to crystallize in two or more different polymorphs or pseudo-polymorphs (Dunitz & Bernstein, 1995; Gavezzotti, 1994), but the factors controlling the choice of form adopted by a particular compound under such varying conditions are still not properly understood. We now report an example of a molecular system in which a change of the recrystallization medium from toluene to dichloromethane results in formation of a solvate, (1), which allows the solvent molecule to occupy a niche in the lattice resulting in high packing symmetry of the molecular unit in the unusual *P*4$_2$*/mbc* space group; only 13 other molecular and coordination compounds have been reported to crystallize in this space group to date (April 1996 version of the Cambridge Structural Database; Allen & Kennard, 1993).



(1)

The molecular unit of (1) is a dimer, $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$, comprising two tricarbonylmanganese fragments connected by a bicyclohexadienyl ligand in which two benzene-derived six-membered rings are connected by a C—C single bond. This molecule can be prepared by reductive dimerization of the $\eta^6$-benzene complex $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ with a single equivalent of the naphthalenide anion; the cation undergoes two-electron reduction to form the $\eta^4$-benzene complex $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$, and if the reductant is added slowly, the cation adds to the anion as it is formed to give (1). Unsolvated (1) crystallizes from toluene in the monoclinic space group *C*2*/c*, with $Z = 4$ and the dimer on a crystallographic twofold axis; we have reported previously the molecular structure of such a crystal (Lee *et al.*, 1996).

Recrystallization of (1) from methylene chloride gives a methylene chloride-solvated pseudo-polymorph of (1) in the tetragonal space group *P*4$_2$*/mbc* (No. 135). A