*Acta Cryst.* (1986). C**42**, 536–538

# Dimethyltin Glycylmethionate

BY HANS PREUT, BRIGITTE MUNDUS AND FRIEDO HUBER

*Fachbereich Chemie, Universität Dortmund, D-4600 Dortmund 50, Postfach 500 500, Federal Republic of Germany*

AND RENATO BARBIERI

*Istituto di Chimica Generale, Gruppo di Chimica dei Composti Organometallici, Università di Palermo, 26–28 Via Archirafi, I-90123 Palermo, Italy*

(*Received* 15 *May* 1985; *accepted* 4 *December* 1985)

**Abstract.** (Glycylmethioninato)dimethyltin, $[Sn(C_7H_{12}N_2O_3S)(CH_3)_2]$, $M_r = 353{\cdot}0$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}662\ (5)$, $b = 11{\cdot}503\ (4)$, $c = 12{\cdot}349\ (4)$ Å, $V = 1372{\cdot}5$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}708$ Mg m$^{-3}$, $\lambda$(Ag $K\alpha$) = 0·56087 Å, $\mu = 1{\cdot}04$ mm$^{-1}$, $F(000) = 704$, $T = 291\ (1)$ K, final $R = 0{\cdot}029$ for 1734 unique reflexions. The polyhedron around Sn is a distorted trigonal bipyramid formed by two equatorial $CH_3$ groups and the tridentate glycylmethioninate ligand, the latter having a nearly planar skeleton. The equatorial Sn–$N_{peptide}$ bond is very short: 2·071 (4) Å. The bond angle O–Sn–$N_{amino}$ is 153·0 (2)°. The molecules are connected through hydrogen bonds between the $NH_2$ group and carbonyl O atoms of two neighbouring molecules.

**Introduction.** Diorganotin glycylglycinates possess antileukaemic activity (Barbieri, Pellerito, Ruisi, Lo Giudice, Huber & Atassi, 1982), as do a series of other diorganotin compounds (Crowe, Smith & Atassi, 1984, and references therein; Huber, Roge, Carl, Atassi, Spreafico, Filippeschi, Barbieri, Silvestri, Rivarola, Ruisi, Di Bianca & Alonzo, 1985). Knowledge of solution-state structures of these compounds is necessary for elucidating structure–activity relationships. During such studies we found that dimethyltin glycylglycinate has the same molecular structure in methanol as in the solid state (Ruisi, Silvestri, Lo Giudice, Barbieri, Lamartina, Atassi, Huber & Grätz, 1985). The solid-state structure with pentacoordinated tin was inferred from Mössbauer and vibrational spectra (Pellerito, Lo Giudice, Ruisi, Bertazzi, Barbieri & Huber, 1976; Barbieri, Pellerito & Huber, 1978) and is in accordance with the structure of solid diphenyltin glycylglycinate (Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977). In water the compound dissolves primarily in the same molecular form, but undergoes slow hydrolysis, initially being in equilibrium with a pentacoordinated intermediate which finally gives dimethyltin oxide (Ruisi *et al.*, 1985). These results demonstrate the general importance of information on solid-state structures of antileukaemic compounds and we therefore started to study structures of relevant compounds. We report in the following the structure of dimethyltin glycylmethioninate, which is a representative example of a dimethyltin dipeptide as well as of a diorganotin dipeptide in which one amino acid group is substituted at the α-carbon atom.

**Experimental.** Preparation by reaction of $(CH_3)_2Sn(OCH_3)_2$ and glycylmethionine in refluxing methanol for 2 h; clear colourless crystals obtained from a solution in methanol on addition of diethyl ether (decomp. >473 K); $\omega/2\theta$ scans, scan speed 2·5° min$^{-1}$ in $\omega$; Nonius CAD-4 diffractometer, graphite-monochromated Ag $K\alpha$ radiation; crystal size 0·22 × 0·42 × 0·26 mm; lattice parameters from least-squares fit with 25 reflexions up to $2\theta = 32{\cdot}2°$; three standard reflexions recorded every 2·5 h showed only random deviations; 2261 reflexions measured in the range $1° \le \theta \le 23°$, max. $(\sin\theta)/\lambda = 0{\cdot}70$ Å$^{-1}$, $0 \le h \le 13$, $0 \le k \le 16$, $0 \le l \le 17$; 2222 unique reflexions, 1734 observed $[I > 3\sigma(I)]$ used for structure determination; intensities corrected for Lorentz–polarization effects and absorption *via* $\psi$ scans, max./min. transmission 1·00/0·91; structure solved with direct methods, $\Delta F$ synthesis and full-matrix least squares on $F$; 146 parameters refined, anisotropic temperature factors for all non-H-atoms, common isotropic temperature factor for all H atoms; H atoms in geometrically calculated positions (C–H 0·95, N–H 0·95 Å), $w^{-1} = [\sigma^2(I) + (0{\cdot}08F_o^2)^2]^{1/2}$, $S = 0{\cdot}83$, $R = 0{\cdot}029$, $wR = 0{\cdot}041$, max. $\Delta/\sigma = 0{\cdot}02$, largest peak in final $\Delta F$ map $\pm 0{\cdot}34\ (9)$ e Å$^{-3}$; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); no correction for secondary extinction; programs: *MULTAN*80 (Main *et al.*, 1980), *Enraf–Nonius Structure Determination Package* (Frenz, 1981), *ORTEP*II (Johnson, 1976), *POP*1 (van de Waal, 1976).

0108-2701/86/050536-03$01.50

**Discussion.** The molecule is shown in Fig. 1 (*ORTEP*II) and a stereoscopic view of the unit cell in Fig. 2 (*POP*1). Atomic parameters are given in Table 1,* selected bond lengths and angles in Table 2. The unit cell contains four molecules. Short intermolecular N···O distances which are markedly shorter than the sum of the van der Waals radii of 3·11 Å (Kitaigorodskii, 1979) indicate hydrogen bonds. With the calculated positions for the two H atoms at N(2), which are placed in tetrahedral positions, two not significantly different H···O distances result, whereas the angles C—O···H and N—H···O are significantly different. These hydrogen-bonding distances and angles are in the same range as those in (L-aspartato)-tris(imidazole)nickel(II) (Battaglia, Bonamartini Corradi, Antolini, Marcotrigiano, Menabue & Pellacani, 1982).

As in diphenyltin glycylglycinate (Huber *et al.*, 1977), which crystallizes in the same space group with nearly the same cell dimensions, the atoms bound to Sn form a distorted trigonal bipyramid. In these two compounds the bond lengths at the Sn atom and in the nearly planar dipeptide skeleton show only in one case [N(2)–C(6)] significant ($\Delta > 3\sigma$) differences. Corresponding bond angles show slight differences, probably because of differences in the packing.

* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42708 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

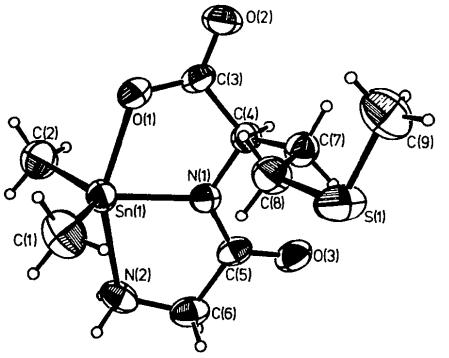


Fig. 1. General view of the molecule.

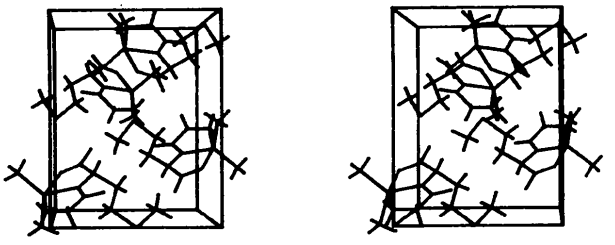

Fig. 2. Stereoscopic view of the unit cell.

It is noteworthy that the Sn(1)–N(1) distance is very short, indicating a strong bond. Actually it is the shortest Sn–N distance hitherto found in organotin(IV) compounds (see Huber *et al.*, 1977) and shorter than the sum of the covalent radii (N = 0·75, Sn = 1·41 Å). The analogous $Sn-N_{peptide}$ bond resists immediate hydrolysis in solutions of dimethyltin glycylglycinate, in

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å² × 10³)

$$U_{eq} = \frac{1}{24\pi^2} \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j .$$

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Sn(1) | −0·03854 (4) | 0·06100 (3) | 0·14887 (3) | 38 |
| S(1) | 0·4916 (2) | −0·1025 (2) | 0·0090 (1) | 65 |
| O(1) | 0·0536 (4) | −0·0638 (3) | 0·2579 (3) | 46 |
| O(2) | 0·2319 (5) | −0·1010 (4) | 0·3624 (3) | 52 |
| O(3) | 0·3123 (5) | 0·2741 (3) | 0·1448 (3) | 51 |
| N(1) | 0·1584 (5) | 0·1264 (4) | 0·1750 (3) | 36 |
| N(2) | −0·0394 (6) | 0·2291 (4) | 0·0559 (4) | 45 |
| C(1) | −0·0590 (8) | −0·0475 (6) | 0·0139 (6) | 67 |
| C(2) | −0·2035 (7) | 0·1036 (8) | 0·2539 (5) | 67 |
| C(3) | 0·1743 (6) | −0·0424 (4) | 0·2933 (4) | 38 |
| C(4) | 0·2526 (5) | 0·0626 (5) | 0·2455 (4) | 36 |
| C(5) | 0·1994 (6) | 0·2250 (5) | 0·1304 (4) | 39 |
| C(6) | 0·0988 (7) | 0·2771 (5) | 0·0494 (5) | 48 |
| C(7) | 0·3813 (6) | 0·0170 (5) | 0·1860 (5) | 44 |
| C(8) | 0·3465 (7) | −0·0613 (6) | 0·0910 (4) | 52 |
| C(9) | 0·588 (1) | −0·1891 (7) | 0·1024 (8) | 79 |

Table 2. *Bond distances* (Å) *and angles* (°) *in* $(CH_3)_2Sn(C_7H_{12}N_2O_3S)$

| | | | |
|---|---|---|---|
| Sn(1)–C(1) | 2·092 (7) | C(4)–C(7) | 1·538 (7) |
| Sn(1)–C(2) | 2·112 (7) | C(7)–C(8) | 1·516 (8) |
| Sn(1)–O(1) | 2·161 (4) | C(8)–S(1) | 1·794 (6) |
| Sn(1)–N(1) | 2·071 (4) | S(1)–C(9) | 1·785 (9) |
| SN(1)–N(2) | 2·249 (4) | N(1)–C(5) | 1·322 (7) |
| O(1)–C(3) | 1·269 (7) | C(5)–O(3) | 1·241 (7) |
| C(3)–O(2) | 1·221 (6) | C(5)–C(6) | 1·518 (8) |
| C(3)–C(4) | 1·543 (7) | C(6)–N(2) | 1·447 (9) |
| C(4)–N(1) | 1·458 (6) | | |

| | | |
|---|---|---|
| H(N2*a*)···O(3) | $(-\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$ | 1·950 (4) |
| H(N2*b*)···O(2) | $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$ | 1·942 (4) |
| N(2)···O(2) | $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$ | 2·881 (6) |
| N(2)···O(3) | $(-\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$ | 2·863 (6) |

| | | | |
|---|---|---|---|
| C(1)–Sn(1)–C(2) | 123·8 (3) | C(3)–C(4)–N(1) | 108·5 (4) |
| C(1)–Sn(1)–N(1) | 115·3 (2) | C(3)–C(4)–C(7) | 108·2 (4) |
| C(1)–Sn(1)–O(1) | 98·0 (2) | N(1)–C(4)–C(7) | 113·0 (4) |
| C(1)–Sn(1)–N(2) | 96·1 (2) | C(4)–C(7)–C(8) | 113·2 (5) |
| C(2)–Sn(1)–N(1) | 120·9 (2) | C(7)–C(8)–S(1) | 114·9 (4) |
| C(2)–Sn(1)–O(1) | 94·7 (2) | C(8)–S(1)–C(9) | 101·0 (4) |
| C(2)–Sn(1)–N(2) | 96·4 (2) | C(4)–N(1)–Sn(1) | 118·9 (3) |
| N(1)–Sn(1)–O(1) | 76·5 (2) | C(4)–N(1)–C(5) | 119·6 (4) |
| N(1)–Sn(1)–N(2) | 76·8 (2) | Sn(1)–N(5)–C(5) | 121·5 (4) |
| O(1)–Sn(1)–N(2) | 153·0 (2) | N(1)–C(5)–O(3) | 126·5 (5) |
| Sn(1)–O(1)–C(3) | 117·7 (3) | N(1)–C(5)–C(6) | 114·9 (5) |
| O(1)–C(3)–C(4) | 118·1 (4) | O(3)–C(5)–C(6) | 118·6 (5) |
| O(1)–C(3)–O(2) | 123·5 (5) | C(5)–C(6)–N(2) | 113·9 (5) |
| O(2)–C(3)–C(4) | 118·4 (5) | C(6)–N(2)–Sn(1) | 110·7 (4) |

| | | |
|---|---|---|
| N(2)–H(N2*a*)···O(3) | $(-\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$ | 160·4 (3) |
| N(2)–H(N2*b*)···O(2) | $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$ | 169·5 (3) |

| | | | |
|---|---|---|---|
| Sn(1)–N(2)–H(N2*a*) | 109·2 (3) | H(N2*a*)–N(2)–H(N2*b*) | 109·4 (5) |
| Sn(1)–N(2)–H(N2*b*) | 109·2 (3) | C(3)–O(2)–H(N2*b*) | 106·3 (4) |
| C(6)–N(2)–H(N2*a*) | 109·2 (5) | C(5)–O(3)–H(N2*a*) | 114·3 (3) |
| C(6)–N(2)–H(N2*b*) | 109·1 (4) | | |

contrast to the two apical bonds of Sn to carboxylate O and amino N (Ruisi *et al.*, 1985).

The support by Fonds der Chemie is gratefully acknowledged.

### References


BARBIERI, R., PELLERITO, L. & HUBER, F. (1978). *Inorg. Chim. Acta*, **30**, L321–L323.

BARBIERI, R., PELLERITO, L., RUISI, G., LO GIUDICE, M. T., HUBER, F. & ATASSI, G. (1982). *Inorg. Chim. Acta*, **66**, L39–L40.

BATTAGLIA, L. P., BONAMARTINI CORRADI, A., ANTOLINI, L., MARCOTRIGIANO, G., MENABUE, L. & PELLACANI, G. C. (1982). *J. Am. Chem. Soc.* **104**, 2407–2411.

CROWE, A. J., SMITH, P. J. & ATASSI, G. (1984). *Inorg. Chim. Acta*, **93**, 179–184.

FRENZ, B. A. (1981). *Enraf–Nonius Structure Determination Package*, 4th ed., version 18.

HUBER, F., HAUPT, H.-J., PREUT, H., BARBIERI, R. & LO GIUDICE, M. T. (1977). *Z. Anorg. Allg. Chem.* **432**, 51–57.

HUBER, F., ROGE, G., CARL, L., ATASSI, G., SPREAFICO, F., FILLIPESCHI, S., BARBIERI, R., SILVESTRI, A., RIVAROLA, E., RUISI, G., DI BIANCA, F. & ALONZO, G. (1985). *J. Chem. Soc. Dalton Trans.* pp. 523–527.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KITAIGORODSKII, A. I. (1979). *Molekülkristalle*. Berlin: Akademie-Verlag.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

PELLERITO, L., LO GIUDICE, M. T., RUISI, G., BERTAZZI, N., BARBIERI, R. & HUBER, F. (1976). *Inorg. Chim. Acta*, **17**, L21–L22.

RUISI, G., SILVESTRI, A., LO GIUDICE, M. T., BARBIERI, R., LAMARTINA, L., ATASSI, G., HUBER, F. & GRÄTZ, K. (1985). *J. Inorg. Biochem.* **25**, 229.

WAAL, B. W. VAN DE (1976). *POP*1. *Plot of Packing Program*. Twente Univ. of Technology, The Netherlands.


*Acta Cryst.* (1986). C**42**, 538–540

# The Structure and the Solid-State $^{113}$Cd NMR of Bis(2-aminomethylpyridine)dinitratocadmium(II)

BY P. F. RODESILER*

*Department of Chemistry, Columbia College, Columbia, South Carolina* 29203, *USA*

AND N. G. CHARLES, E. A. H. GRIFFITH, K. LEWINSKI† AND E. L. AMMA‡

*Department of Chemistry, University of South Carolina, Columbia, South Carolina* 29208, *USA*

(*Received* 2 *January* 1985; *accepted* 3 *December* 1985)

**Abstract.** $[Cd(NO_3)_2(C_6H_8N_2)_2]$, $M_r = 452{\cdot}70$, monoclinic, $P2_1/c$, $a = 9{\cdot}020\ (2)$, $b = 8{\cdot}970\ (1)$, $c = 10{\cdot}231\ (1)$ Å, $\beta = 101{\cdot}80\ (1)°$, $V = 810{\cdot}3\ (4)$ Å$^3$, $Z = 2$, $D_m = 2{\cdot}0$–$1{\cdot}8$ (with decomposition), $D_x = 1{\cdot}86$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 13{\cdot}84$ cm$^{-1}$, $F(000) = 452$, $T \sim 293$ K, $R = 0{\cdot}063$, 2171 observed reflections. The structure may be described as isolated bis(2-aminomethylpyridine)dinitratocadmium(II) entities separated by ordinary van der Waals distances. The Cd atom is on a crystallographic center of symmetry. The coordination polyhedron of Cd is that of a *trans* $CdN_4O_2$ system in which the four N atoms come from the two 2-aminomethylpyridine ligands and the O atoms are from monodentate nitrate groups. The Cd–N distances are 2·326 (2) Å (pyridine N) and 2·279 (2) Å (amino N). The Cd–O distance is 2·450 (3) Å. There is an approximately 7° tilt of the O–Cd–O line relative to the normal of the $CdN_4$ equatorial plane. The $^{113}$Cd CP/MAS solid-state signal is observed at 222 p.p.m. deshielded from the 0·1 mol dm$^{-3}$ $Cd(ClO_4)_2$ in $D_2O$ standard.

**Introduction.** $^{113}$Cd NMR has been shown to be a versatile tool for the observation of metal sites in a wide variety of chemical and biological compounds (Rodesiler, Turner, Charles, Griffith & Amma, 1984; Ellis, 1983, and references therein; Armitage & Otvos, 1982, and references therein). The development of solid-state cross-polarization magic-angle spinning (CP/MAS) $^{113}$Cd NMR has even further enhanced the potential utility of this metal-ion probe (Ackerman, Orr, Bartuska & Maciel, 1979; Mennitt, Shatlock, Bartuska

* Deceased March 1985.

† Permanent address: Jagiellonian University, Krakow, Poland.

‡ To whom correspondence should be addressed.

0108-2701/86/050538-03$01.50