

from the University Grants Commission, New Delhi, is also gratefully acknowledged.

References

- DAN, J., SETH, S. & CHAKRABORTY, S. (1989). *Acta Cryst.* **C45**, 1018–1021.
- DUTTA, R. L. & DAS, B. R. (1984). *Indian J. Chem.* **23A**, 654–656.
- DUTTA, R. L. & HOSSAIN, MD. M. (1984). *Indian J. Chem.* **23A**, 30–32.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- SEAL, A. & RAY, S. (1984). *Acta Cryst.* **C40**, 929–932.
- SETH, S. & CHAKRABORTY, S. (1984). *Acta Cryst.* **C40**, 1530–1533.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- VICKERY, B. L., BRIGHT, D. & MALLINSON, P. R. (1971). *XRAYARC*. IBM 1130 program system, modified for a Cyber computer.

Acta Cryst. (1993). **C49**, 873–875

Structure of Di(*n*-butyl)bis(morpholinocarbodithioato- κ^2S,S')tin(IV)

BY V. VRÁBEL AND E. KELLÖ

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava, Czechoslovakia

(Received 14 May 1992; accepted 10 December 1992)

Abstract. $[\text{Sn}(\text{C}_4\text{H}_9)_2(\text{C}_5\text{H}_8\text{NOS}_2)_2]$, $M_r = 557.41$, monoclinic, $C2/c$, $a = 17.152$ (14), $b = 7.146$ (5), $c = 20.995$ (28) Å, $\beta = 93.00$ (9)°, $V = 2570$ (4) Å³, $Z = 4$, $D_m = 1.43$ (2), $D_x = 1.44$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.32$ mm⁻¹, $F(000) = 1144$, room temperature, $R = 0.057$ for 1895 unique observed reflections. The structure consists of discrete hexacoordinated tin complexes. The geometry around the Sn atom is distorted octahedral with two anisobidentate dithiocarbamate-like (dtc) ligands in equatorial positions and two C atoms of the butyl groups in axial positions. The dtc ligand has a short Sn—S(1) distance of 2.525 (2) Å and longer Sn—S(2) of 3.001 (3) Å. The Bu—Sn—Bu angle is 139.7 (2)°.

Introduction. Great attention has been paid to the study of crystal structures of dtc complexes in the past few years. Interest has centred on their practical applications (Hagihara & Yamashita, 1966; Klug, 1966) and on the nature of the metal–ligand bonding. According to the X-ray studies the geometry about the Sn atom is strongly distorted from the *trans* octahedral one seen in diorganotin(IV)–dtc complexes (Morris & Schlemper, 1979*a,b*; Lockhart, Manders, Schlemper & Zuckerman, 1986; Lokaj, Kellö, Kettmann, Vrábel & Rattay, 1986). The largest deviations from octahedral geometry are due to the steric requirements of the four-membered chelate rings. In a continuing effort to understand the coordination chemistry of such complexes we

have now determined the crystal structure of di(*n*-butyl)bis(morpholinocarbodithioato- κ^2S,S')tin(IV).

Experimental. The title compound was synthesized as reported previously (Vrábel, Lokaj, Kellö, Garaj, Batsanov & Struchkov, 1992). On recrystallization from *n*-heptane colourless needle-like crystals were obtained. Analysis found: N, 5.08; C, 38.89; H, 6.14%. Calculated: N, 5.03; C, 38.79; H, 6.15%. Density measured by flotation (in ZnSO₄ solution). Data collected on a crystal of size 0.35 × 0.15 × 0.3 mm. Space group $C2/c$ from systematic absences: hkl , $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Approximate values of lattice parameters from rotation and Weissenberg patterns. Accurate lattice parameters were refined by least squares on the basis of 15 precisely centred reflections with $4 < 2\theta < 11^\circ$ on a Syntex $P2_1$ four-circle diffractometer using Mo $K\alpha$ radiation filtered by a graphite monochromator. Intensities of 2959 unique reflections ($R_{int} = 0.034$) collected in the range $2\theta < 55^\circ$, $h = 0$ to 22, $k = 0$ to 8, $l = -25$ to 26 by $\theta/2\theta$ scans, variable rate 4.9 to 29.3° min⁻¹ in 2θ , background to scan time ratio 1.0, scan width 2° plus $\alpha_1 - \alpha_2$ dispersion. No significant variation in intensities of two standard reflections (202, 402) measured after 98 reflections. Data reduction performed with the program *XP21* (Pavelčík, 1987). All intensities corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved by the heavy-

atom method and refined on F by block-diagonal least squares using 1895 observed reflections with $I > 1.96\sigma(I)$. H atoms located at calculated positions; their coordinates and thermal parameters were fixed. Positional and anisotropic thermal parameters for non-H atoms were refined to $R = 0.057$, $wR = 0.059$ and $S = 0.925$, 125 variables, $(\Delta/\sigma)_{\max} = 0.3$, $w = (a + |F_o| + b|F_o|^2)^{1/2}$, where $a = 8.0$, $b = 0.007$. Maximum and minimum heights in the final difference Fourier synthesis 0.54 and $-0.47 \text{ e } \text{\AA}^{-3}$, respectively. Scattering factors for uncharged atoms taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1982) using an M4030 computer at the Slovak Technical University, Bratislava, Czechoslovakia.

Discussion. Positional parameters of non-H atoms and B_{eq} values are listed in Table 1,* bond lengths and angles are in Table 2. The molecular geometry and atom numbering are shown in Fig. 1.

The crystal structure consists of discrete monomeric molecules in which the Sn atom is located on the twofold axis. The coordination polyhedron is a strongly distorted octahedron with four S atoms chelated to the Sn atom. Each of the dtc ligands has short Sn—S(1) 2.525 (2) Å and long Sn—S(2) 3.001 (3) Å bonds. The long distance is significantly less than the sum of the van der Waals radii (4.0 Å; Bondi, 1964). The Sn—C(6) distance [2.134 (5) Å] completes the coordination polyhedron. C atoms of the two butyl groups are located between *cis*- and *trans*-octahedral positions with C—Sn—C angle of 139.7 (2)°. The S—Sn—S bond angles deviate from 90°, ranging between 64.5 (1)° in the chelate ring and 148.5 (1)° for the S(2)—Sn—(2) bond between ligands. The coordination geometry of the SnC_2S_4 core and the associated bond lengths are remarkably similar to those of $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$ (Kimura, Yasuoka, Kasai & Kakudo, 1972), $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ (Lockhart, Manders & Schlemper, 1985), $(n\text{-Bu})_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$ (Lokaj *et al.*, 1986) and $(n\text{-Bu})_2\text{Sn}(\text{S}_2\text{CNET}_2)_2$ (Vrabel *et al.*, 1992). The S_2CN fragment is planar within experimental error, the Sn atom deviating by -0.264 (4) Å from this plane. In $[\text{Cl}(\text{Me}_2\text{dtc})_2\text{SnCH}_2\text{CHC}_2\text{OOCH}_3]$ (Jung, Jeong & Sohn, 1990) the dtc ligands are bidentate, the Sn—S distances ranging between 2.535 (3) and 2.635 (3) Å, C and Cl atoms occupying *cis* positions [C—Sn—Cl is 93.6 (3)°].

Table 1. Final positional parameters for non-H atoms ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

	x	y	z	B_{eq}
Sn	5000	6362 (1)	2500	5.08 (7)
S(1)	5381 (1)	3711 (2)	1784 (1)	6.50 (8)
S(2)	5661 (1)	7507 (2)	1263 (1)	6.02 (7)
O(1)	6573 (3)	2572 (7)	-0356 (2)	9.7 (2)
N(1)	6095 (4)	4342 (7)	0746 (2)	9.1 (2)
C(1)	5757 (3)	5154 (7)	1207 (2)	6.4 (2)
C(2)	6268 (6)	2270 (12)	0716 (3)	12.6 (3)
C(3)	6173 (6)	1591 (11)	0111 (4)	11.2 (3)
C(4)	6410 (6)	4397 (14)	-0321 (3)	12.4 (3)
C(5)	6500 (6)	5403 (13)	0248 (3)	12.7 (3)
C(6)	6080 (3)	7391 (7)	2912 (3)	6.1 (1)
C(7)	6114 (3)	9489 (8)	2915 (3)	7.6 (2)
C(8)	6928 (4)	10258 (10)	3205 (3)	8.8 (2)
C(9)	6990 (4)	12258 (12)	3267 (5)	12.1 (3)

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Sn—S(1)	2.525 (2)	N(1)—C(2)	1.512 (10)
Sn—S(2)	3.001 (3)	N(1)—C(5)	1.492 (10)
Sn—C(6)	2.134 (5)	C(2)—C(3)	1.362 (11)
S(1)—C(1)	1.740 (5)	C(4)—C(5)	1.396 (10)
S(2)—C(1)	1.694 (5)	C(6)—C(7)	1.500 (8)
O(1)—C(3)	1.412 (10)	C(7)—C(8)	1.592 (9)
O(1)—C(4)	1.337 (11)	C(8)—C(9)	1.438 (11)
N(1)—C(1)	1.292 (7)		
S(1)—Sn—S(2)	64.5 (1)	C(1)—N(1)—C(2)	124.6 (6)
S(1)—Sn—S(2) ⁱ	147.2 (1)	S(2)—C(1)—N(1)	123.2 (4)
S(1)—Sn—C(6)	104.7 (2)	S(1)—C(1)—N(1)	116.9 (4)
S(1)—Sn—C(6) ^j	105.3 (2)	S(1)—C(1)—S(2)	119.9 (4)
S(1)—Sn—S(1) ^j	82.8 (1)	N(1)—C(2)—C(3)	111.9 (7)
S(2)—Sn—S(2) ^j	148.5 (1)	O(1)—C(3)—C(2)	115.6 (8)
C(6)—Sn—C(6) ⁱ	139.7 (2)	O(1)—C(4)—C(5)	122.4 (8)
Sn—S(1)—C(1)	95.0 (2)	N(1)—C(5)—C(4)	107.7 (7)
Sn—S(2)—C(1)	80.3 (2)	Sn—C(6)—C(7)	112.3 (4)
C(3)—O(1)—C(4)	109.6 (6)	C(6)—C(7)—C(8)	112.3 (5)
C(2)—N(1)—C(5)	111.6 (6)	C(7)—C(8)—C(9)	115.9 (6)
C(1)—N(1)—C(5)	122.7 (6)		

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

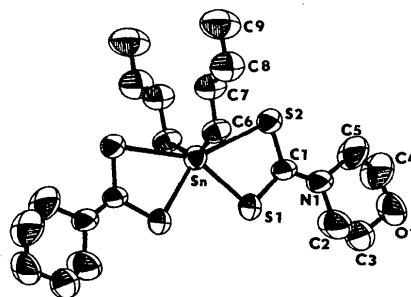


Fig. 1. Molecular structure of the title compound with the atom-labelling scheme.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). *NRC Crystallographic Programs for the IBM360 System*. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55853 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1017]

- BONDI, A. J. (1964). *J. Phys. Chem.* **68**, 441–452.
 HAGIHARA, H. & YAMASHITA, S. (1966). *Acta Cryst.* **21**, 350–358.
 JUNG, O.-S., JEONG, J. H. & SOHN, Y. S. (1990). *Acta Cryst.* **C46**, 31–33.
 KIMURA, T., YASUOKA, N., KASAI, N. & KAKUDO, M. (1972). *Bull. Chem. Soc. Jpn.* **45**, 1649–1654.
 KLUG, H. P. (1966). *Acta Cryst.* **21**, 536–546.
 LOCKHART, T. P., MANDERS, W. F. & SCHLEMPER, E. O. (1985). *J. Am. Chem. Soc.* **107**, 7451–7453.
 LOCKHART, T. P., MANDERS, W. F., SCHLEMPER, E. O. & ZUCKERMAN, J. J. (1986). *J. Am. Chem. Soc.* **108**, 4074–4078.
 LOKAJ, J., KELLÖ, E., KETTMANN, V., VRÁBEL, V. & RATTAY, V. (1986). *Collect. Czech. Chem. Commun.* **51**, 2521–2527.
 MORRIS, J. S. & SCHLEMPER, E. O. (1979a). *J. Cryst. Mol. Struct.* **9**, 1–12.
 MORRIS, J. S. & SCHLEMPER, E. O. (1979b). *J. Cryst. Mol. Struct.* **9**, 13–31.
 NARDELLI, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis*. Univ. of Parma, Italy.
 PAVELČÍK, F. (1987). *XP21. A Computer Program for Syntax P2, Data Reduction*. Department of Analytical Chemistry, Faculty of Pharmacy, J. A. Komenský Univ., 83232 Bratislava, Czechoslovakia.
 VRÁBEL, V., LOKAJ, J., KELLÖ, E., GARAJ, J., BATSANOV, A. C. & STRUCHKOV, YU. T. (1992). *Acta Cryst.* **C48**, 633–635.

Acta Cryst. (1993). **C49**, 875–878

Structure of a Lead(II) Complex of a New 13-Membered Macrocyclic Ligand with Two Pendant Carboxymethyl Groups

BY MICHIKO B. INOUE* AND QUINTUS FERNANDO†

Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA

AND CARMEN A. VILLEGAS AND MOTOMICHI INOUE†

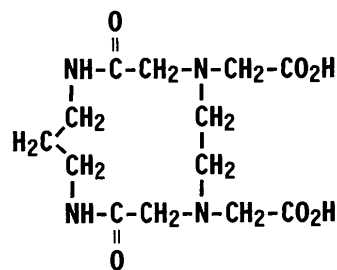
CIPM, Universidad de Sonora, Apdo. Postal 130, Hermosillo, Sonora, Mexico

(Received 12 June 1992; accepted 24 December 1992)

Abstract. (Aqua)[2,9-dioxo- κ^2O,O' -1,4,7,10-tetraaza- κ^2N^4,N^7 -4,7-cyclotridecanediacetato(2-)- κ^2O,O']-lead(II) dihydrate, $[\text{Pb}(\text{C}_{13}\text{H}_{20}\text{N}_4\text{O}_6)(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, $M_r = 589.56$, monoclinic, $P2_1/c$, $a = 8.999$ (1), $b = 23.055$ (1), $c = 9.382$ (1) Å, $\beta = 108.58$ (1)°, $V = 1845.1$ (4) Å³, $Z = 4$, $D_x = 2.12$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 92.6$ cm⁻¹, $F(000) = 1144$, $T = 294$ K, $R = 0.026$ for 2829 independent reflections with $I > 3\sigma(I)$. A Pb^{II} ion is coordinated to six atoms from a macrocyclic ligand and an O atom from water. An additional weak coordination bond with an O atom from an adjacent metal chelate molecule results in a binuclear structure. The resulting eight-coordination geometry around a Pb^{II} ion is an unusually distorted triangulated dodecahedron.

Introduction. The coordination chemistry of macrocyclic ligands with pendant functional groups has attracted a growing interest (Bernhardt & Lawrance, 1990; Parker, 1990). In our previous study, new 12-membered and 24-membered macrocycles with pendant carboxymethyl groups were synthesized by condensation of ethylenediaminetetraacetic dianhydride with ethylenediamine, and the copper(II)

and the manganese(II) complexes of these ligands were characterized by X-ray crystal analyses (Inoue, Villegas, Asano, Nakamura, Inoue & Fernando, 1992). These metal chelates have novel molecular structures due to the coordination of the amide O atoms. The structure of a metal chelate with a macrocyclic ligand is sensitively dependent on the relative sizes of the metal and the macrocycle. In the present study we have synthesized a new 13-membered macrocycle (I) by a condensation between 1,3-propanediamine and ethylenediaminetetraacetic dianhydride, and carried out an X-ray study of its Pb^{II} complex. The coordination polyhedron around the Pb^{II} ion is found to be unusually distorted due to the nature of the coordinated ligand.



(I)

* Visiting scientist from the Universidad de Sonora.

† To whom correspondence should be addressed.