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

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
U	0.5000	0.0	0.5000	0.039 (1)
N(1)	0.1030 (11)	−0.0944 (6)	0.1453 (10)	0.067 (3)
N(2)	0.1523 (10)	0.0760 (4)	0.5187 (10)	0.051 (3)
O(1)	0.1752 (8)	0.0522 (4)	0.3823 (7)	0.059 (2)
O(2)	0.2862 (9)	0.0671 (4)	0.6525 (7)	0.056 (2)
O(3)	0.0062 (11)	0.1081 (5)	0.5269 (9)	0.073 (3)
O(4)	0.3660 (8)	−0.0248 (4)	0.2057 (7)	0.054 (2)
O(5)	0.4168 (9)	−0.0900 (4)	0.5466 (8)	0.053 (2)
C(1)	0.2481 (12)	−0.0666 (5)	0.1034 (10)	0.048 (3)
C(2)	0.2769 (14)	−0.0866 (6)	−0.0673 (11)	0.058 (3)
C(3)	0.317 (2)	−0.1718 (9)	−0.0862 (16)	0.095 (6)
C(4)	0.132 (3)	−0.2229 (8)	−0.1359 (19)	0.109 (7)
C(5)	0.026 (3)	−0.2227 (8)	0.003 (2)	0.119 (8)
C(6)	−0.0473 (19)	−0.1450 (9)	0.0391 (14)	0.090 (5)

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

The geometry of caprolactam is given in square brackets (Oya & Myasnikova, 1974).

U—O(1)	2.506 (6)	U—O(2)	2.556 (7)
U—O(4)	2.360 (5)	U—O(5)	1.752 (7)
N(2)—O(1)	1.239 (11)	N(2)—O(2)	1.262 (8)
N(2)—O(3)	1.239 (12)	N(1)—C(6)	1.490 (15) [1.48]
N(1)—C(1)	1.313 (13) [1.23]	O(4)—C(1)	1.253 (10) [1.25]
C(1)—C(2)	1.504 (13) [1.51]	C(2)—C(3)	1.514 (19) [1.52]
C(3)—C(4)	1.59 (2) [1.53]	C(4)—C(5)	1.55 (3) [1.53]
C(5)—C(6)	1.51 (2) [1.50]		
O(1)—U—O(2)	49.9 (2)	O(2)—U—O(4)	115.6 (2)
O(1)—U—O(4)	65.8 (2)	O(2)—U—O(5)	89.3 (3)
O(1)—U—O(5)	92.2 (2)	O(2)—U—O(2*a*)	180.0 (1)
O(1)—U—O(1*a*)	180.0 (1)	O(4)—U—O(5)	89.1 (2)
O(4)—U—O(4*a*)	180.0 (1)	O(5)—U—O(5*a*)	180.0 (1)
O(1)—N—O(3)	122.7 (7)	O(1)—N(2)—O(2)	117.2 (8)
U—O(1)—N(2)	98.0 (4)	O(2)—N(2)—O(3)	120.0 (8)
U—O(4)—C(1)	142.7 (6)	U—O(2)—N(2)	94.9 (5)
C(1)—N(1)—C(6)	127.1 (9) [125.0]	O(4)—C(1)—C(2)	119.3 (9)
N(1)—C(1)—C(2)	119.9 (9) [119.5]	N(1)—C(1)—O(4)	120.7 (8) [121.0]
C(1)—C(2)—C(3)	113.6 (9) [112.5]	C(2)—C(3)—C(4)	112.3 (12) [114]
C(3)—C(4)—C(5)	113.3 (12) [114.5]	C(4)—C(5)—C(6)	115.5 (13) [114.5]
N(1)—C(6)—C(5)	112.3 (12) [114]		

An HNO_3 solution (3 *M*) of $UO_2(NO_3)_2$ was extracted by caprolactam dissolved in petroleum ether (b.p. 333-363 K) at room temperature until the organic phase was saturated by the compound. The yellowish precipitate formed was washed with deionized water and petroleum ether successively. A crystal suitable for X-ray diffraction studies was obtained by recrystallization from toluene solution. Seven reflections with $I \geq 15000$ in the range $10 < \theta < 45°$ were selected to collect azimuthal (ψ scan) data. The increment in the azimuthal angle ψ was 10° each time so that 36 data were collected for each reflection and the total 252 data were used to model and define the pseudo ellipsoid which was then used to calculate the absorption corrections; maximum $(\sin\theta/\lambda) = 0.596$ Å^{-1}. The crystal structure was solved by the heavy-atom method and developed from electron-density syntheses. The coordinates of non-H atoms and isotropic thermal vibration parameters were then refined by least squares. Anisotropic thermal vibration parameters were then introduced. All the above calculations were performed on an Eclipse/S140 computer using the *SHELXTL* program (Sheldrick, 1986). The least-squares method used was the block-diagonal matrix approximation.

Lists of structure factors and anisotropic thermal parameter have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71305 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1002]

References

Fleming, J. E. & Lynton, H. (1960). *Chem. Ind.* (*London*), pp. 1415-1416.

Hall, D., Rac, A. D. & Waters, T. N. (1965). *Acta Cryst.* **24**, 389-391.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Musikas, C. (1988). *Sep. Sci. Technol.* **22**, 1211-1218.

Oya, Kh. P. & Myasnikova, P. M. (1974). *Zh. Strukt. Khim.* **15**, 680–685.

Reynolds, J. G., Zalkin, A. & Templeton, D. H. (1977). *Inorg. Chem.* **16**, 3357-3359.

Sheldrick, G. M. (1985). *SHELXTL User's Manual.* Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1993). C**49**, 1943–1945

Structure of Dibenzylchlorotin(IV) Thiooxinate

E. KELLÖ AND V. VRÁBEL

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Czechoslovakia

A. LYČKA

Research Institute of Organic Syntheses, 532 18 Pardubice, Czechoslovakia

J. SIVÝ

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, 832 32 Bratislava, Czechoslovakia

(*Received* 18 *November* 1992; *accepted* 25 *March* 1993)

Abstract

The structure of dibenzylchloro(8-quinolinethiolato-*N*,*S*)tin(IV) consists of monomeric trigonal bipyramidal chelate molecules. The two benzyl C atoms and the thiooxinate S atom occupy equatorial sites; the N atom of the bidentate thiooxinate group [Sn—N 2.367 (4) Å] and the Cl atom [Sn—Cl 2.475 (2) Å] are axial. The strong Sn—N bond causes deformation of the coordination polyhedron and is a consequence of electronic effects of the thiooxinate group and steric effects of the benzyl substituents.

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

Comment

There is little information available with regard to crystal-structure determinations of organotin(IV) oxinates and thiooxinates. Here we report the crystal structure of $Bz_2Sn^{IV}(Cl)txin$ (txin = 8-quinolinethiolate). The results of ^{119}Sn, ^{15}N and ^{13}C NMR studies on diorgano(chloro)tin(IV) oxinates and thiooxinates compared with those obtained by ^{119}Sn CP/MAS spectroscopy confirm that there is an interaction between a nucleus with spin number $I = \frac{1}{2}$ with two different quadrupolar nuclei ^{14}N ($I = 1$) and ^{35}Cl and/or ^{37}Cl ($I = \frac{3}{2}$) (Lyčka, Holeček, Sebald & Tkáč, 1991); these authors suggested that in the title complex the Sn centre is five-coordinate.

The compound was synthesized as reported previously (Lyčka, Jirman, Holeček & Tkáč, 1989) and single crystals were obtained by slow evaporation from a $CDCl_3/CH_3OH$ solution at room temperature.

The molecular structure and the atom-numbering scheme are shown in Fig. 1. The structure of the title compound consists of monomeric chelate molecules. The Sn atom is trigonal bipyramidal with the Cl and N atoms in apical positions. The thiooxinate group also bonds to the metal through the S atom. The Sn—S(1) [2.386 (2) Å] and Sn—N(1) [2.367 (4) Å] bond distances are nearly equal and significantly shorter than those found in triphenyltin(IV) thiooxinate [Sn—S 2.434 Å average, Sn···N 2.602 Å average (Furmanova, Struchkov, Rokhlina & Kravtsov, 1980)] or in triphenyltin(IV) thiophenolate [Sn—S 2.420 (8) Å (Bokij, Struchkov, Kravtsov & Rokhlina, 1974)]. The strong Sn—N bonded ligand causes deformation of the coordination polyhedron and is a consequence of electronic effects of the thiooxinate group and steric effects of the benzyl substituents on the Sn atom. The C(1) and C(8) atoms of the benzyl groups and the S atom define the equatorial plane of the trigonal bipyramid with the Sn atom located 0.047 (2) Å above this plane. The Cl(1)—Sn—N(1) angle [166.2 (1)°] is in good agreement with those found in triphenyltin(IV) thiooxinate [C—Sn—N 168.7 (3) and 164.4 (4)°].

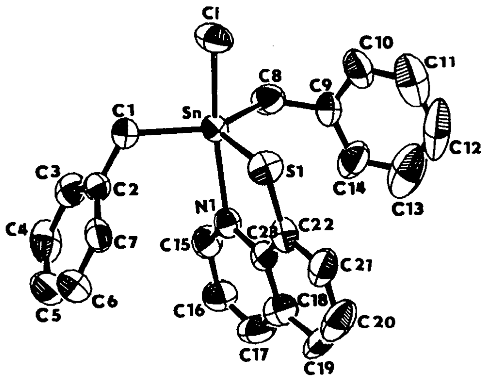

Fig. 1. Perspective drawing of the title compound and atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

Spectroscopic data are completely in accordance with the crystal structure; a strong intramolecular coordination between the Sn atom and the N atom of the thiooxinate group is observed in both solution and in the solid state.

Experimental

Crystal data

$[SnCl(C_9H_6NS)(C_7H_7)_2]$
$M_r = 496.621$
Monoclinic
$P2_1/c$
$a = 10.192$ (6) Å
$b = 10.695$ (9) Å
$c = 19.501$ (9) Å
$\beta = 99.38$ (4)°
$V = 2097.2$ Å^3
$Z = 4$
$D_x = 1.57$ Mg m^{-3}
$D_m = 1.55$ (2) Mg m^{-3}
Density measured by flotation in $ZnSO_4$ solution

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 5$-9°
$\mu = 1.45$ mm^{-1}
$T = 293$ K
Needle
0.45 × 0.20 × 0.10 mm
Yellow
Crystal source: crystallization from $CDCl_3/CH_3OH$

Data collection

$XP2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.675$, $T_{max} = 0.988$
4990 measured reflections
4848 independent reflections

1368 observed reflections [$I > 1.96\sigma(I)$]
$R_{int} = 0.043$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -25 \rightarrow 24$
2 standard reflections
intensity variation: <5%

Refinement

Refinement on F
Final $R = 0.046$
$wR = 0.048$
$S = 0.925$
1368 reflections
244 parameters
H-atom parameters not refined

$w = [\sigma^2(F_o) + 0.02|F_o|^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.632$ e Å^{-3}
$\Delta\rho_{min} = -0.285$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Sn(1)	0.04210 (4)	0.19770 (4)	0.22410 (2)	3.91 (1)
Cl(1)	−0.1301 (1)	0.2845 (2)	0.2866 (1)	5.35 (6)
S(1)	0.0452 (2)	0.3957 (2)	0.1680 (1)	4.81 (5)
N(1)	0.2041 (4)	0.1630 (4)	0.1520 (2)	3.38 (13)
C(1)	0.1765 (5)	0.1819 (6)	0.3202 (2)	3.97 (17)
C(2)	0.3156 (5)	0.1473 (5)	0.3167 (2)	3.61 (17)
C(3)	0.3595 (6)	0.0261 (6)	0.3298 (3)	4.65 (20)

C(4)	0.4892 (6)	−0.0056 (6)	0.3259 (3)	5.75 (22)
C(5)	0.5735 (6)	0.0796 (7)	0.3077 (3)	6.84 (27)
C(6)	0.5326 (6)	0.1998 (8)	0.2936 (3)	7.06 (26)
C(7)	0.4039 (5)	0.2301 (5)	0.2984 (3)	4.35 (18)
C(8)	−0.0861 (5)	0.0653 (6)	0.1651 (3)	4.58 (21)
C(9)	−0.1497 (5)	0.1260 (6)	0.0991 (3)	4.64 (20)
C(10)	−0.2685 (6)	0.1893 (6)	0.0966 (3)	5.65 (20)
C(11)	−0.3243 (7)	0.2487 (6)	0.0377 (4)	8.17 (28)
C(12)	−0.2621 (8)	0.2485 (7)	−0.0178 (4)	9.21 (29)
C(13)	−0.1415 (8)	0.1841 (7)	−0.0180 (3)	8.89 (30)
C(14)	−0.0889 (6)	0.1241 (7)	0.0429 (3)	5.91 (22)
C(15)	0.2685 (5)	0.0601 (5)	0.1526 (3)	4.23 (18)
C(16)	0.3511 (6)	0.0331 (6)	0.1042 (3)	5.04 (22)
C(17)	0.3611 (5)	0.1192 (6)	0.0536 (3)	5.41 (20)
C(18)	0.2901 (5)	0.2296 (5)	0.0510 (3)	4.30 (20)
C(19)	0.2966 (6)	0.3230 (6)	0.0002 (3)	6.06 (23)
C(20)	0.2284 (7)	0.4281 (6)	0.0031 (3)	6.65 (25)
C(21)	0.1511 (6)	0.4507 (6)	0.0537 (3)	5.61 (22)
C(22)	0.1436 (5)	0.3635 (5)	0.1046 (3)	4.04 (19)
C(23)	0.2127 (5)	0.2554 (5)	0.1032 (2)	3.69 (17)

Table 2. *Geometric parameters* (Å, °)

Sn(1)—S(1)	2.386 (2)	Sn(1)—C(1)	2.139 (5)
Sn(1)—N(1)	2.367 (4)	Sn(1)—C(8)	2.133 (6)
Sn(1)—Cl(1)	2.475 (5)		
S(1)—Sn(1)—N(1)	78.7 (1)	S(1)—Sn(1)—Cl(1)	87.5 (1)
C(1)—Sn(1)—C(8)	131.9 (2)	C(1)—Sn(1)—S(1)	114.7 (2)
C(1)—Sn(1)—Cl(1)	90.2 (2)	C(1)—Sn(1)—N(1)	95.7 (2)
C(8)—Sn(1)—S(1)	113.2 (2)	C(8)—Sn(1)—Cl(1)	95.3 (2)
C(8)—Sn(1)—N(1)	90.0 (2)	Cl(1)—Sn(1)—N(1)	166.2 (1)

Data reduction was performed with the program $XP2_1$ (Pavelčik, 1987). The structure was solved by the Patterson method and refinement was on *F* by block-diagonal least squares. H atoms were located at calculated positions; their coordinates and thermal parameters were fixed. Calculations were performed with a local version of the *NRC* (Ahmed, Hall, Pippy & Huber, 1973) system and *PARST* (Nardelli, 1984).

This research was supported financially by the Ministry of Science and Education.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71214 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1027]

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.

Bokij, N. G., Struchkov, Yu. T., Kravtsov, D. N. & Rokhlina, E. M. (1974). *Zh. Strukt. Chim.* **15**, 497–503.

Furmanova, N. G., Struchkov, Yu. T., Rokhlina, E. M. & Kravtsov, D. N. (1980). *Zh. Strukt. Chim.* **21**, 87–93.

Lyčka, A., Holeček, J., Sebald, A. & Tkáč, I. (1991). *J. Organomet. Chem.* **409**, 331–339.

Lyčka, A., Jirman, J., Holeček, J. & Tkáč, I. (1989). *J. Organomet. Chem.* **372**, 327–338.

Nardelli, M. (1984). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis.* Univ. of Parma, Italy.

Pavelčik, F. (1987). *A Computer Program for Syntex $P2_1$ Data Reduction.* Department of Analytical Chemistry, Faculty of Pharmacy, J. A. Komenský Univ., 832 32 Bratislava, Czechoslovakia.

Acta Cryst. (1993). C**49**, 1945–1947

Facile Synthesis and Structure of the Mn^{IV}–Mn^{IV} Dinuclear Complex $[Mn(salpn)O]_2(DMSO)_2$ [$salpnH_2$ = *N*,*N*′-bis(salicylidene)-1,3-diaminopropane]

Nadeem Aurangzeb, Charles A. McAuliffe,*
Robin G. Pritchard and Michael Watkinson

Department of Chemistry, University of Manchester
Institute of Science and Technology,
Manchester M60 1QD, England

Manuel Bermejo, Ana Garcia-Deibe and
Antonio Sousa

Departmento de Quimica Inorganica, Universidad de
Santiago de Compostela, Spain

(*Received* 26 *August* 1992; *accepted* 18 *December* 1992)

Abstract

The Mn^{IV} dimer $[Mn(salpn)O]_2$, di-μ-oxo-bis({2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato-*N*,*N*′,*O*,*O*′}manganese(IV)), has been produced as the DMSO adduct by the facile air oxidation of the complex $\{[Mn^{III}(salpn)(H_2O)](ClO_4)\}_2$ in DMSO, giving dark-green crystals. Both Mn atoms are in approximately octahedral environments made up of the tetradentate Schiff base salpn and two μ-oxo O atoms, which are both *cis* [Mn—O 1.804 (5) and Mn—O′ 1.832 (5) Å].

Comment

Manganese plays a vital role in a number of metalloproteins (Dismukes, 1986). Of these metalloproteins the most important is undoubtedly the dioxygen envolving complex (OEC) of photosystem II (PSII) found in green plants (Dismukes, 1986; Pecoraro, 1988). It is now well established that in PSII four Mn atoms are essential for high rates of dioxygen evolution, although the precise configuration of the active site is still not known (Pecoraro, 1988). Extended X-ray absorption fine structure (EXAFS) studies of the OEC shows that there is at least one, and possibly two short Mn···Mn distances of ~2.7 Å (George, Prince & Cramer, 1989). A number of model complexes have been synthesized, with mononuclear Mn (Dutta, Basu & Chakravorty 1991), dinuclear Mn (Ashmawy, McAuliffe, Parish & Tames, 1985; Wieghardt *et al.*, 1986; Bonadies *et al.*, 1989) and higher nuclearity Mn (Perlepes, Huffman & Christou, 1991). Our own studies have centred on