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Tricymantrenyltin Oxide: Synthesis and Structure

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Abstract—Tricymantrenyltin oxide $\{[C_5H_4Mn(CO)_3]_3Sn\}_2O$ (**I**) is synthesized in a yield of 72% by the reaction of tricymantrenyltin chloride with sodium hydroxide in an acetone–water solution. The structure of the synthesized compound is studied by IR spectroscopy and X-ray diffraction (XRD) (CIF file CCDC no. 2044007). The IR spectrum of complex **I** exhibits characteristic absorption bands attributed to stretching vibrations of carbonyl groups at 1921 and 2019 cm^{-1}. According to the XRD data, the tin atoms in compound **I** have a distorted tetrahedral coordination: the CSnC angles are 102.3(2)°–120.1(2)°, the Sn–C bond lengths are 2.107(6)–2.119(7) Å, and the Sn–O distances are 1.945(4) and 1.959(4) Å. The structural organization of the crystal in complex **I** is controlled by intermolecular bonds C–H···O≡C (2.57–2.71 Å).

Keywords: tricymantrenyltin oxide, synthesis, structure, XRD

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INTRODUCTION

Organic compounds of tin are known to be efficient stabilizers of polyvinyl chloride and catalysts for the reactions of the OH-containing compounds with isocyanates [1], among which the organic derivatives of tetravalent tin with the general formulas R_4Sn, R_2SbX_2, and R_3SbX (X is the electronegative ligand) are presented most widely [2]. It can be expected that the properties of the organotin derivatives would not change upon the replacement of alkyl or aryl substituents at the tin atom by cymantrenyl groups. Note that the cymantrenyl compounds are known for elements of the broad series: Li [3], Hg [4], B [5, 6], Ni [7], Ge, Pb [8], Ag [9], Cu [10], Au [11], P [12], Ti [13], and Sb [14, 15]. However, similar tin(IV) compounds with cymantrenyl radicals are presented in the literature by single examples [16–19]. For instance, among the cymantrenyltin derivatives dicymantrenyltin dichloride $[C_5H_4Mn(CO)_3]_2SnCl_2$ [16] and tricymantrenyltin chloride $[C_5H_4Mn(CO)_3]_3SnCl$ [19] are known. The first derivative was prepared from dicymantrenylmercury and tin(IV) dichloride, and the second compound was synthesized from cymantrenyllithium and tin(IV) chloride in a yield of 73% [19]. The synthesis of tricymantrenyltin chloride from dicymantrenyltin dichloride and cymantrenyllithium was also described [20].

Continuing the study of methods for the synthesis of cymantrenyltin derivatives, we studied the reaction of tricymantrenyltin chloride with sodium hydroxide.

EXPERIMENTAL

Tricymantrenyltin chloride was synthesized using a described procedure [20]. Prior to synthesis, solvents (reagent grade) were dried over calcium chloride and distilled.

Synthesis of tricymantrenyltin oxide $\{[C_5H_4Mn(CO)_3]_3Sn\}_2O$ (I). A solution of sodium hydroxide (0.144 g, 3.60 mmol) in water (100 mL) was added to a solution of tricymantrenyltin chloride (0.486 g, 0.6 mmol) in acetone (20 mL), and the mixture was stirred for 5 min. After 24 h, a light yellow precipitate was filtered off, washed with distilled water, and dried. Pale yellow crystals were isolated from recrystallization from benzene in a yield of 0.337 g (72%), T_{decomp} = 204°C.

For $C_{48}H_{24}O_{19}Mn_6Sn_2$		
Anal. calcd., %	C, 39.18	H, 1.64
Found, %	C, 39.12	H, 1.67

IR (ν, cm^{-1}): 3116, 2019, 1921, 1402, 1199, 1150, 1028, 839, 768, 667, 632, 538.

The IR spectrum was recorded on a Shimadzu IRAffinity-1S FT-IR spectrometer in KBr pellets.

XRD of the crystal of complex **I** was carried out on a D8 Quest diffractometer (Bruker, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [21]. All calculations on structure determination and refine-

Table 1. Crystallographic data and experimental and structure refinement parameters for complex **I**

Parameter	Value
Empirical formula	$C_{48}H_{24}O_{19}Mn_6Sn_2$
FW	1471.69
T, K	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.651(6)
b, Å	35.000(16)
c, Å	12.927(7)
α, deg	90.00
β, deg	113.44(3)
γ, deg	90.00
V, Å^3	5251(4)
Z	4
ρ_{calc}, g/cm^3	1.861
μ, mm^{-1}	2.401
F(000)	2856.0
Crystal size, mm	0.69 × 0.53 × 0.33
Data collection range over θ, deg	5.78–54.4
Ranges of reflection indices	$-16 \le h \le 16$, $-44 \le k \le 44$, $-16 \le l \le 16$
Measured reflections	50910
Independent reflections	11625
Refinement variables	676
GOOF	1.122
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0596$, $wR_2 = 0.1321$
R factors for all reflections	$R_1 = 0.0698$, $wR_2 = 0.1381$
Residual electron density (min/max), e/Å^3	−2.57/4.29

Table 2. Selected bond lengths and bond angles in the structure of complex **I**

Bond	*d*, Å	Angle	ω, deg
Sn(1)–O(10)	1.945(4)	O(10)Sn(1)C(1)	102.3(2)
Sn(1)–C(1)	2.107(6)	C(1)Sn(1)C(11)	108.6(3)
Sn(1)–C(11)	2.122(8)	C(1)Sn(1)C(21)	120.1(2)
Sn(1)–C(21)	2.115(7)	C(21)Sn(1)C(11)	108.2(3)
Sn(2)–O(10)	1.959(4)	O(10)Sn(2)C(31)	105.9(2)
Sn(2)–C(31)	2.110(6)	O(10)Sn(2)C(41)	104.8(3)
Sn(2)–C(41)	2.119(7)	O(10)Sn(2)C(51)	107.4(2)
Sn(2)–C(51)	2.111(6)	C(31)Sn(2)C(41)	115.2(3)

ment were performed using the SHELXL/PC [22] and OLEX2 [23] programs. The structure was solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement results for complex **I** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC

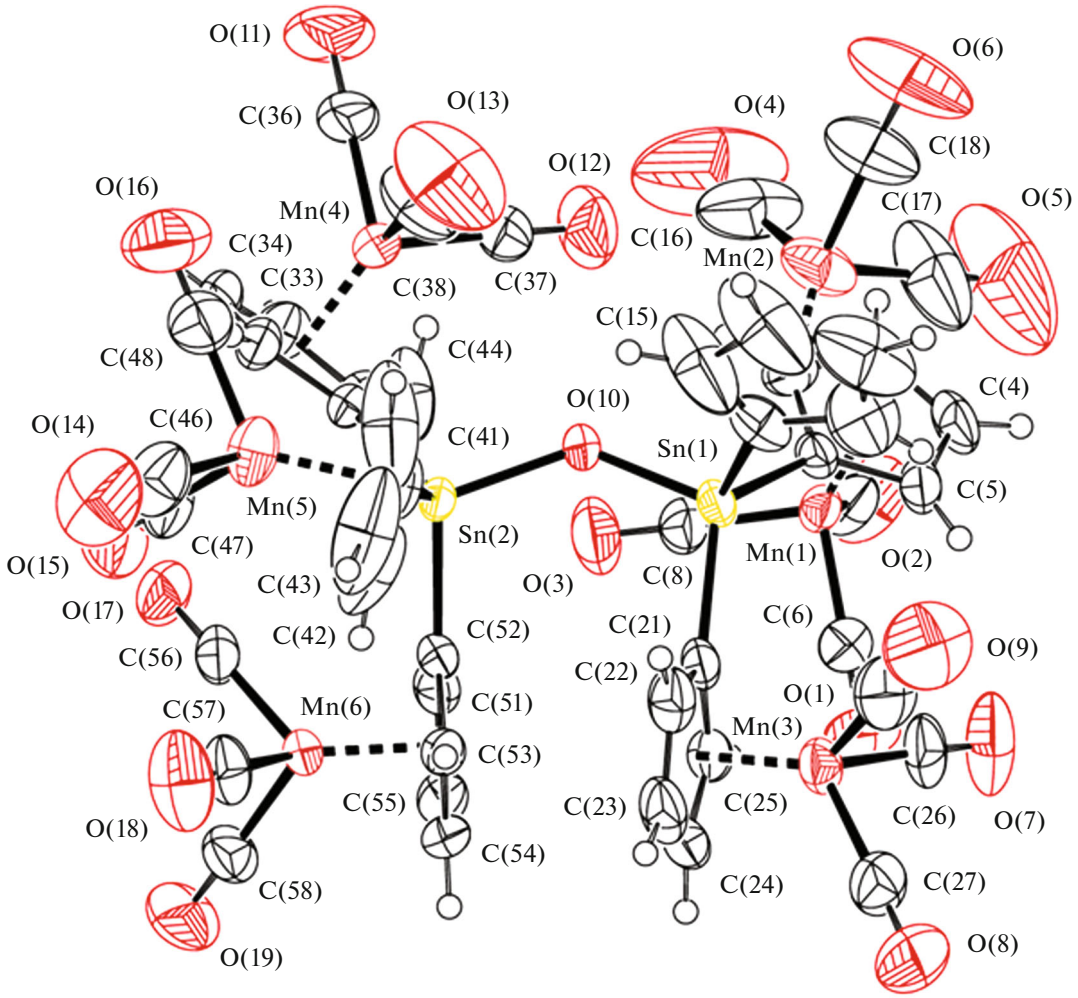

Fig. 1. Structure of compound **I**.

no. 2044007; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

It is known that the reaction of cymantrenyllithium in a tetrahydrofuran solution with dicymantrenyltin(IV) dichloride (molar ratio 1 : 1) or of cymantrenyllithium with tin chloride (molar ratio 4 : 1) affords tricymantrenyltin chloride [20]. An increase in the cymantrenyllithium concentration in the reaction medium does not lead to the formation of tetracymantrenyltin, which can be explained by steric hindrances caused by the presence of three large (bulky) cymantrenyl ligands in tricymantrenyltin chloride. Note that a possibility of similar steric hindrances was indicated for the reaction of tricymantrenylantimony with iodine [15].

We studied the reaction of tricymantrenyltin chloride with sodium hydroxide hoping to obtain tricymantrenyltin hydroxide. However, tricymantrenyltin oxide $\{[C_5H_4Mn(CO)_3]_3Sn\}_2O$ (**I**) was found to be the single product of the reaction that occurred in an aqueous solution of acetone.

$$2\left[C_5H_4Mn\left(CO\right)_3\right]_3SnCl + 2NaOH \rightarrow \left\{\left[C_5H_4Mn\left(CO\right)_3\right]_3Sn\right\}_2O + 2NaCl + H_2O\ (\mathbf{I})$$

Complex **I** represents light yellow crystals, whose structure was studied by IR spectroscopy and XRD. The IR spectrum of the complex exhibits characteristic absorption bands assigned to stretching vibrations of carbonyl groups at 1921 and 2019 cm^{-1}, which somewhat differ from the corresponding absorption

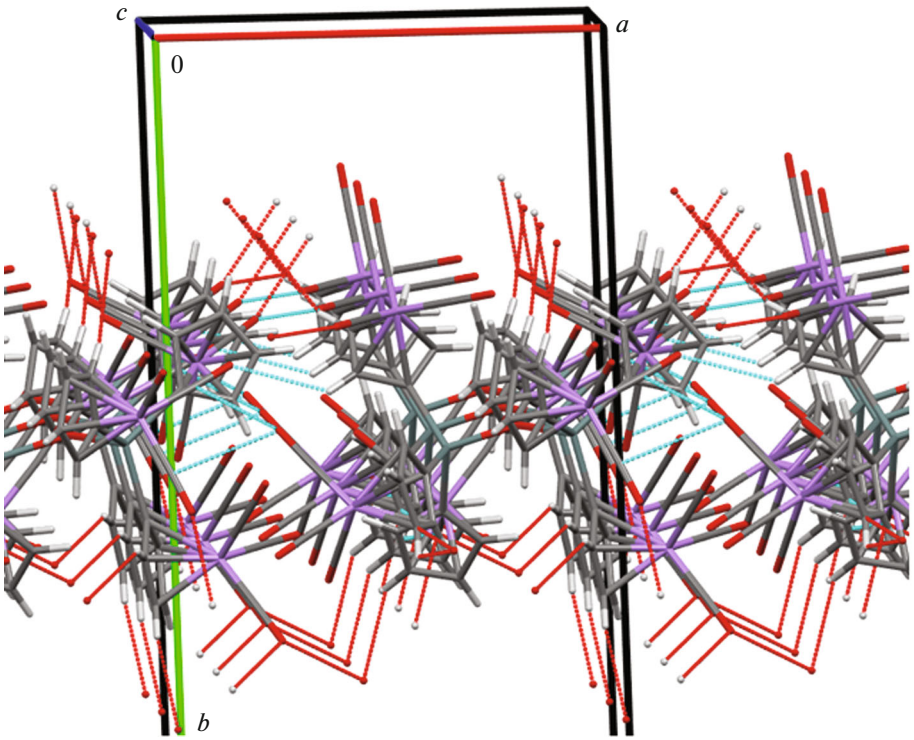

Fig. 2. Packing of molecules in the crystal of compound **I** (projection along the crystallographic *c* axis).

bands in the spectrum of cymantrene (1943 and 2025 cm^{-1}) [24].

According to the XRD data, the tin atom in the molecule of compound **I** (Fig. 1) has a tetrahedral coordination (the CSnC and OSnC angles vary in ranges of 102.3(2)°–120.1(2)° and 102.3(3)°–109.6(2)°, respectively). The binuclear molecule of compound **I** is bent (the SnOSn angle is 133.2(5)°), and the cymantrenyl ligands at the tin atoms are turned by the carbonyl groups from the bridging oxygen atom. The Sn–C bond lengths vary in an narrow range of 2.107(6)–2.119(7) Å. The Sn–O distances are 1.945(4) and 1.959(4) Å, which is less than the sum of covalent radii of tin and oxygen atoms (2.05 Å) [25].

The structural organization of the crystal in complex **I** is controlled by numerous intermolecular contacts C–H···O≡C (2.57–2.71 Å) involving the hydrogen and oxygen atoms, which are close to the sum of their van der Waals radii (2.62 Å [26]). The molecules are packed in stacks oriented along the crystallographic *c* axis (Fig. 2).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. *Khimicheskaya entsiklopediya* (Chemical Encyclopedia), Knunyants, I.L., Ed., vol. 1, Moscow: Sov. Entsikl., 1988.
2. Kocheshkov, K.A., Zemlyanskii, N.N., Sheverdina, N.I., and Panov, E.M., *Metody elementoorganicheskoi khimii. Germanii, olovo, svinets* (Methods of Organoelement Chemistry. Germanium, Tin, Lead), Moscow: Nauka, 1968.
3. Nesmeyanov, A.N., Anisimov, K.N., Kolobova, R.E., and Makarov, Yu.V., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1968, vol. 17, no. 3, p. 686.
4. Nesmeyanov, A.N., Anisimov, K.N., and Valueva, Z.P., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1962, vol. 11, no. 9, p. 1683.
5. Renk, T., Ruf, W., and Siebert, W., *J. Organomet. Chem.*, 1976, vol. 120, no. 1, p. 1. https://doi.org/10.1016/S0022-328X(00)80400-3
6. Nesmeyanov, A.N., Kolobova, R.E., Makarov, Yu.V., and Anisimov, K.N., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1969, vol. 18, no. 9, p. 1992.
7. Nesmeyanov, A.N., Perevalova, E.G., Khomik, L.T., and Leont'eva, L.I., *Dokl. Akad. Nauk SSSR*, 1973, vol. 209, no. 4, p. 869.
8. Nesmeyanov, A.N., Anisimov, K.N., Kolobova, R.E., and Makarov, Yu.V., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1973, vol. 22, no. 12, p. 2815.
9. Nesmeyanov, A.N., Sazonova, V.A., and Sedova, N.N., *Dokl. Akad. Nauk SSSR.*, 1971, vol. 198, no. 3, p. 590.
10. Nesmeyanov, A.N., Sazonova, V.A., and Sedova, N.N., *Dokl. Akad. Nauk SSSR*, 1972, vol. 202, no. 2, p. 362.

11. Nesmeyanov, A.N., Grandberg, K.I., Baukova, T.V., et al., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1969, vol. 18, no. 9, p. 2032.
12. Nesmeyanov, A.N., Anisimov, K.N., and Valueva, Z.P., *Dokl. Akad. Nauk SSSR*, 1974, vol. 216, no. 1, p. 106.
13. Daroda, R.J., Wilkinson, G., Hursthouse, M.B., et al., *J. Chem. Soc., Dalton Trans.*, 1980, no. 11, p. 2315. https://doi.org/10.1039/DT9800002315
14. Saf'yanov, Yu.N., Kuz'min, E.A., and Sharutin, V.V., *Kristallografiya*, 1984, vol. 29, no. 5, p. 928.
15. Sharutin, V.V., Sharutina, O.K., Senchurin, V.S., and Andreev, P.V., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 5, p. 1049.
16. Nesmeyanov, A.N., Tolstaya, T.P., and Korol'kov, V.V., *Dokl. Akad. Nauk SSSR*, 1973, vol. 209, no. 5, p. 1113.
17. Nesmeyanov, A.N., Tolstaya, T.P., Korol'kov, V.V., and Yarkevich, A.N., *Dokl. Akad. Nauk SSSR*, 1975, vol. 221, no. 6, p. 1337.
18. Bokii, N.G. and Struchkov, Yu.T., *Koord. Khim.*, 1978, vol. 4, no. 1, p. 134.
19. Zakharov, L.N., Andrianov, V.G., Struchkov, Yu.T., et al., *Koord. Khim.*, 1980, vol. 6, no. 5, p. 1104.
20. Sharutin, V.V. and Senchurin, V.S., *Vestnik YuUrGU. Ser. Khim.*, 2018, vol. 10, no. 4, p. 75. https://doi.org/10.14529/chem180408
21. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Madison: Bruker AXS Inc., 1998.
22. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Madison: Bruker AXS Inc., 1998.
23. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339. https://doi.org/10.1107/S0021889808042726
24. Nesmeyanov, A.N., Dvoryantseva, G.G., Pustyl'nik, Zh.P., et al., *Dokl. Akad. Nauk SSSR*, 1967, vol. 174, no. 2, p. 368.
25. Cordero, B., Gómez, V., Platero-Prats, A.E., et al., *Dalton Trans.*, 2008, no. 21, p. 2832. https://doi.org/10.1039/B801115J
26. Mantina, M., Chamberlin, A.C., Valero, R., et al., *J. Phys. Chem. A*, 2009, vol. 113, no. 19, p. 5806. https://doi.org/10.1021/jp8111556

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