O22—C22	1.243 (2)	C2—N3	1.325 (2)
O21—C22	1.257 (2)	C22—C21	1.531 (2)
N5—O5	1.290 (2)	C4—N4	1.311 (2)
N5—C5	1.338 (2)	C4—N3	1.346 (2)
C6—O6	1.221 (2)		
O2W—Zn1—O3W	92.69 (5)	O5—N5—C5	117.75 (15)
O2W—Zn1—O1W	91.24 (6)	O22—C22—O21	125.21 (17)
O3W—Zn1—O1W	89.92 (6)		
N2—C21—C22—O21	−179.32 (15)	N2—C21—C22—O22	0.1 (2)

Symmetry code: (i) $-x, -y, -z$.

Table 2. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···O22	0.81 (3)	2.22 (3)	2.903 (2)	142 (3)
O1W—H1WA···O4W	0.88 (3)	1.99 (3)	2.776 (2)	148 (3)
O2W—H2WA···O22^i	0.84 (3)	1.89 (3)	2.729 (2)	172 (3)
O2W—H2WB···O5^{ii}	0.88 (3)	1.79 (2)	2.6662 (19)	176 (2)
O3W—H3WA···O21^i	0.86 (2)	1.79 (2)	2.6415 (19)	170 (2)
O3W—H3WB···O21^{iii}	0.86 (2)	1.88 (2)	2.728 (2)	172 (2)
O4W—H4WA···O6^{iv}	0.85 (3)	2.12 (3)	2.905 (2)	153 (3)
N2—H2···O3W^v	0.86	2.27	3.086 (2)	159.3
N4—H4A···O5	0.85 (3)	1.94 (3)	2.613 (2)	135 (3)
N4—H4B···O6^{vi}	0.93 (3)	1.92 (3)	2.749 (2)	147 (2)

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

H atoms were placed at their calculated positions (C—H 0.96 Å) and were refined at the final cycle, except for the H atoms on N2, C21 and C1.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *PLUTON* (Spek, 1995). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1042). Services for accessing these data are described at the back of the journal.

References

Arranz Mascarós, P. (1997). Thesis, University of Jaén, Spain.
Arranz Mascarós, P., Godino Salido, M. L., López Garzón, R., Gutierrez Valero, M. L. & Moreno, J. M. (1999). *Polyhedron*, **18**, 793–797, and references therein.
Arranz Mascarós, P., López Garzón, R., Godino Salido, M. L. & Gutierrez Valero, M. D. (1998). *Transition Met. Chem.* **23**, 501–505.
Bonamartini Corradi, A. (1992). *Coord. Chem. Rev.* **117**, 45–98.
Goldberg, A. L. & Dice, J. F. (1974). *Ann. Rev. Biochem.* **43**, 852.
Haurowitz, F. (1963). *The Chemistry and Function of Protein*, p. 909. New York: Academic Press.
Loktinova, L. A. & Pegg, A. E. (1996). *Cancer Res.* **56**, 1578–1583.
Low, J. N., Ferguson, G., López, R., Arranz, P., Cobo, J., Melguizo, M., Nogueras, M. & Sánchez, A. (1997). *Acta Cryst.* C53, 890–892.
Mak, T. C. W. & Huang, S.-H. (1987). *Polyhedron*, **6**, 1111–1114.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
Pegg, A. E., Swenn, K., Chaen, M. Y., Dolan, M. E. & Moschel, R. C. (1995). *Biochem. Pharmacol.* **50**, 1141–1148.
Photaki, I. (1974). *Topics in Sulfur Chemistry*, Vol. 1, edited by A. Sunning, p. 111. Stuttgart: Thieme.
Roy, S. K., Moschel, R. C. & Dolan, M. E. (1996). *Drug Metab. Diagnos.* **24**, 1205–1211.
Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *XSCANS. X-ray Single-Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1995). *PLUTON. Molecular Graphics Program*. University of Utrecht, The Netherlands.

Bis(2-ethyl-3-hydroxy-4-pyranonato)diiodotin(IV) acetonitrile solvate

Zaisheng Lu,^{a} John Burgess,^{b} John Fawcett^b and David R. Russell^b

^{a}Department of Chemistry, Xuzhou Normal University, Xuzhou 221009, Jiangsu, People's Republic of China, and ^{b}Department of Chemistry, University of Leicester, Leicester LE1 7RH, England. E-mail: jxf@leicester.ac.uk

Abstract

In the title compound, $[SnI_2(C_7H_7O_3)_2]\cdot C_2H_3N$, the ligand donor atoms are arranged around the Sn atom in a distorted octahedron, with the iodide ligands *cis* with respect to one another. The acetonitrile molecule of crystallization occupies interstitial positions in the structure.

Comment

The tin–ligand bond distances, some of the angles subtended by ligand donor atoms at tin, and carbon–oxygen and carbon–carbon bond distances in the chelate rings of the coordinated 2-ethyl-3-hydroxy-4-pyranonate (ethyl-maltolate, etma) ligands in the title compound, bis(2-ethyl-3-hydroxy-4-pyranonato)diiodotin(IV) acetonitrile solvate, (I), are given in Table 1. The structure of

(I)
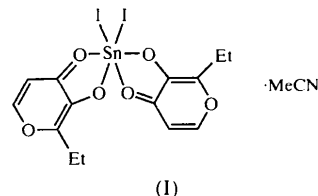
Sn(etma)$_2$I$_2$ (Fig. 1) is, as expected, similar to that of its chloro analogue Sn(etma)$_2$Cl$_2$ (Alsheri *et al.*, 1999). In both cases, the geometry around the Sn atom is approximately octahedral, with the halide ligands in *cis* positions. There is, however, a difference in the relative disposition of the two etma ligands. In Sn(etma)$_2$I$_2$,

one iodide is *trans* to a hydroxy-O atom and the other is *trans* to a keto-O atom, whereas in Sn(etma)$_2$Cl$_2$, both chlorides are *trans* to keto-O atoms, and the two hydroxy-O atoms are thus *trans* to each other and the two keto-O atoms are *cis* to each other. So whereas the two tin–chlorine bonds in Sn(etma)$_2$Cl$_2$ are equivalent and equal in length, the tin–iodide bond *trans* to the hydroxy-O atom in Sn(etma)$_2$I$_2$ is significantly longer than that *trans* to the keto-O atom. The angle subtended at tin by the two iodides is slightly larger (1.5°) than that subtended by the two chlorides in Sn(etma)$_2$Cl$_2$, consistent with the greater bulk of the iodide ligands. Differences between the tin–oxygen distances, chelate bite angles, and carbon–carbon and carbon–oxygen bond distances in the chelate rings of the two compounds are not statistically significant, so there is no detectable difference between the extent of delocalization in the chelate rings of Sn(etma)$_2$I$_2$ and Sn(etma)$_2$Cl$_2$.
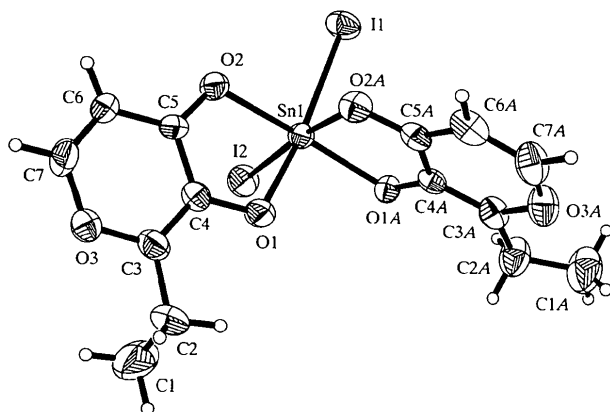

Fig. 1. The molecular structure of (I) showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii and the acetonitrile solvate molecule has been omitted.

The ethyl groups of the maltolate ligands exhibit high anisotropic displacement parameters perpendicular to the C—C bonds, which are typically found for this ligand even when data are measured at low temperature. The most anisotropic atom is C1 and as a consequence the apparent C1—C2 bond distance is 1.327 Å. A riding-model bond-length correction (Johnson, 1970) gives a value of 1.503 Å.

The acetonitrile molecule of crystallization occupies interstitial positions in the structure and does not interact significantly with surrounding Sn(etma)$_2$I$_2$ molecules.

Experimental

The title compound was prepared by adding a solution of tin(IV) iodide (1.56 g) in anhydrous dichloromethane (40 ml) dropwise, with stirring, to a solution of 2-ethyl-3-hydroxy-4-pyranone (ethylmaltol, 1.00 g) in anhydrous dichloromethane (15 ml). The reaction mixture was refluxed for 3 h and

then filtered. The filtrate was allowed to cool to laboratory temperature, then further cooled in a refrigerator to obtain crystals suitable for X-ray analysis.

Crystal data

[SnI$_2$(C$_7$H$_7$O$_3$)$_2$]·C$_2$H$_3$N
M_r = 691.80
Monoclinic
$P2_1/n$
a = 7.658 (1) Å
b = 25.364 (4) Å
c = 11.500 (2) Å
β = 95.17 (1)°
V = 2224.6 (6) Å^3
Z = 4
D_x = 2.066 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 37 reflections
θ = 5.30–12.47°
μ = 3.952 mm^{-1}
T = 293 (2) K
Needle
0.59 × 0.12 × 0.11 mm
Yellow

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction:
ψ scan (*SHELXTL/PC*;
Sheldrick, 1996)
T_{min} = 0.181, T_{max} = 0.647
5084 measured reflections
3911 independent reflections
2730 reflections with
$I > 2\sigma(I)$

R_{int} = 0.031
θ_{max} = 25°
h = $-1 \rightarrow 9$
k = $-1 \rightarrow 30$
l = $-13 \rightarrow 13$
3 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.098
S = 1.042
3911 reflections
238 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 1.5444P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = -0.55 e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn1—O1	2.054 (5)	O1—C4	1.351 (8)
Sn1—O1A	2.067 (4)	O2—C5	1.274 (8)
Sn1—O2	2.127 (5)	C4—C5	1.411 (10)
Sn1—O2A	2.130 (5)	O1A—C4A	1.321 (8)
Sn1—I2	2.7298 (9)	O2A—C5A	1.281 (9)
Sn1—I1	2.7417 (8)	C4A—C5A	1.426 (9)
O1—Sn1—O1A	90.03 (19)	O2—Sn1—I2	96.68 (15)
O1—Sn1—O2	79.20 (19)	O2A—Sn1—I2	174.02 (15)
O1A—Sn1—O2	162.81 (19)	O1—Sn1—I1	169.56 (15)
O1—Sn1—O2A	86.2 (2)	O1A—Sn1—I1	97.55 (13)
O1A—Sn1—O2A	79.25 (18)	O2—Sn1—I1	91.71 (14)
O2—Sn1—O2A	86.6 (2)	O2A—Sn1—I1	88.17 (14)
O1—Sn1—I2	89.54 (16)	I2—Sn1—I1	96.67 (3)
O1A—Sn1—I2	96.58 (12)		

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

References

Alsheri, S., Burgess, J., Fawcett, J. & Russell, D. R. (1999). *Polyhedron*. Submitted.

Fait, J. (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Johnson, J. (1970). *Crystallographic Computing*, pp. 220–226. Copenhagen: Munksgaard.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Sheldrick, G. M. (1996). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C55, 2053–2055

(Acetonitrile-*N*)(η⁴-2-methylbuta-1,3-diene)(η⁵-pentamethylcyclopentadienyl)-ruthenium(II) trifluoromethanesulfonate

Christian Gemel,[a] Karl Kirchner,[a] Roland Schmid[a] and Kurt Mereiter[b]

[a]*Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria, and* [b]*Institute of Mineralogy, Crystallography and Structural Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria. E-mail: kmereite@fbch.tuwien.ac.at*

Abstract

The title compound, [Ru{η⁵-C₅(CH₃)₅}{η⁴-CH₂C(CH₃)-CHCH₂}(CH₃CN)](CF₃SO₃) or [Ru(C₅H₈)(C₁₀H₁₅)-(C₂H₃N)](CF₃SO₃), contains a half-sandwich ruthenium complex with an *exo*-oriented π-bonded diene moiety inclined at an angle of 16.0 (2)° to the cyclopentadienyl ring. The coordination geometry of ruthenium can be described as a three-legged piano stool.

Comment

Nucleophilic attack at metal-coordinated ligands is an important route in synthetic organic chemistry for obtaining new regio- and stereoselective functionalized molecules (Collman *et al.*, 1987). Such a process is particularly facile when the metal center is coordinatively saturated, substitutionally inert and sufficiently electron deficient, and when the ligand to be attacked is a conjugated or non-conjugated olefin (Davies *et al.*,

1978). Thus, cationic complexes of the type [Ru(η⁵-Cp*)(η⁴-diene)(CH₃CN)]⁺ (Cp* is pentamethylcyclopentadienyl) are expected to react readily with nucleophiles to give 3-allyl complexes and constitute a good model system for mechanistic studies. In this context and in the context of related work (Gemel *et al.*, 1996, 1997), the title compound, (acetonitrile-*N*)(η⁴-2-methylbuta-1,3-diene)(η⁵-pentamethylcyclopentadienyl)-ruthenium(II) trifluoromethanesulfonate, (I), was studied by X-ray diffraction.

(I)
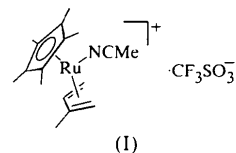
A view of (I) is shown in Fig. 1. The Ru—C bond lengths exhibit a comparatively narrow spread of 2.180 (3)–2.241 (3) Å for the cyclopentadienyl moiety and 2.173 (3)–2.242 (3) Å for the 2-methylbutadiene moiety. A moderate asymmetry in the Ru—C bond lengths (Table 1) should stem from repulsive interactions between the methyl groups of Cp* and the 2-methylbutadiene moiety. The Cp* moiety shows mean values for cyclic and exocyclic C—C bonds of 1.426 (14) and 1.504 (4) Å, respectively. The 2-methylbutadiene moiety is *exo*-oriented and adopts a staggered configuration relative to the Cp* unit. The angle between the least-squares planes through the cyclopentadienyl ring and the 2-methylbutadiene C atoms is 16.0 (2)°. The diene exhibits the expected short–long–short pattern of bond lengths (Table 1). Its terminal CH₂ groups were refined with respect to H-atom positions and adopt orientations indicating that the Ru atom polarizes the diene π-electron system considerably and alters the hybridization of C11 and C14 from pure sp^2 in the free diene towards sp^3 in the π-bonded diene [note that the CH₂ groups in Fig. 1 are distinctly inclined to the diene least-squares plane by 34 (2)° for C11H₂ and 35 (2)° for C14H₂]. This corroborates earlier findings on two related neutral complexes, namely [Ru(η⁵-Cp*)-(η⁴-butadiene)(η¹-OSO₂CF₃)] and [Ru(η⁵-Cp*)(η⁴-butadiene)(η¹-OCOCF₃)] (Gemel *et al.*, 1997), which also show a staggered orientation of butadiene *versus* Cp*, but which display larger inclination angles between the Cp* and butadiene moieties of 20.2 and 19.7°, respectively. It should be mentioned that the *exo*-orientation of the butadiene in the title compound and these two complexes is controlled by the electron configuration at the divalent ruthenium center. In corresponding complexes of tetravalent ruthenium, *e.g.* [Ru(η⁵-Cp*)(η⁴-2,3-dimethylbutadiene)Br₂]⁺ (Gemel *et al.*, 1996), the butadiene moiety is reverted relative to Fig. 1, *i.e.* with the terminal C atoms of the butadiene on the left side of the figure and the inner C atoms on the right side (*endo* orientation). In compounds of this type, the inclination