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A 1:1 Adduct of Aquachlorotriphenyltin with 3,4,7,8-Tetramethyl-1,10-phenanthroline

SEIK WENG NG

Institute of Advanced Studies, University of Malaya, 59100 Kuala Lumpur, Malaysia

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Abstract

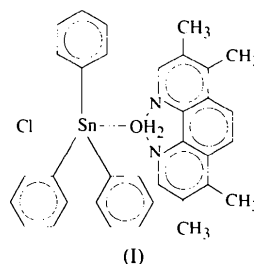
The aquaorganotin moiety in the title adduct, [SnCl(C₆H₅)₃(H₂O)].C₁₆H₁₆N₂, is linked by hydrogen bonds through its axially bonded water molecule to the substituted 1,10-phenanthroline moiety. The Sn atom has *trans*-trigonal bipyramidal coordination, with aqua and chloro ligands in the axial positions.

Comment

With 1,10-phenanthroline, triphenyltin chloride forms a dimeric hydrated complex in which the coordinated water molecule [Sn—O = 2.42 Å] is linked by hydrogen bonds (O···N = 2.96 and 3.02 Å) to two

1,10-phenanthroline bases. Each base is further linked, although much more weakly (O···N = 3.31 and 3.42 Å), to the water molecule of another aquachlorotriphenyltin moiety (Gabe, Lee & Smith, 1984).

Addition of four methyl substituents to the 1,10-phenanthroline ligand increases the basicity of its N atoms, enhancing the propensity for hydrogen bonding with the water of the aquachlorotriphenyltin molecule. Thus, as shown by this present study, 3,4,7,8-tetramethyl-1,10-phenanthroline forms much shorter hydrogen bonds [2.661 (3) and 2.767 (3) Å] with aquachlorotriphenyltin than does 1,10-phenanthroline. The complex, (I), exists as a monomeric molecule and the



shortest water–water O···O distance exceeds 3.5 Å. Bond dimensions involving the Sn atom are similar to those found in the 1,10-phenanthroline and 2,2':6',2''-terpyridyl complexes. However, the hydrogen bonds are shorter and the Sn—O bond longer than those [O···N = 2.766 (2) and 2.807 (2); Sn—O = 2.317 (2) Å] found in the terpyridyl complex, which is monomeric. In the terpyridyl complex, the water molecule binds the 1- and 1''-N atoms of the base (Prasad, Lee, Le Page & Smith, 1982).

The Sn atom has essentially regular trigonal bipyramidal coordination geometry, with the three phenyl groups equatorial and the aqua and chloro ligands in the axial positions.

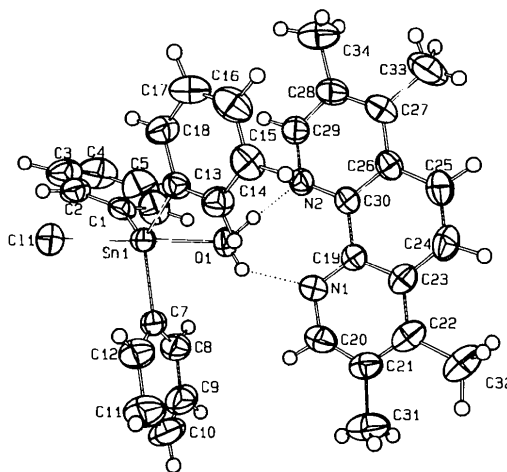


Fig. 1. Atomic labelling scheme for the title compound. Ellipsoids are drawn at the 50% probability level.

Experimental

A hot ethanol solution containing stoichiometric quantities of triphenyltin chloride and 3,4,7,8-tetramethyl-1,10-phenanthroline precipitated large crystals of the complex when cooled slowly.

Crystal data

[SnCl(C₆H₅)₃(H₂O)]₂·

C₁₆H₁₆N₂

M_r = 639.79

Monoclinic

*P*2₁/*n*

a = 16.373 (4) Å

b = 10.4066 (6) Å

c = 17.629 (5) Å

β = 90.101 (14)°

V = 3003.8 (12) Å³

Z = 4

D_s = 1.415 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 12–13°

μ = 0.968 mm⁻¹

T = 298 K

Cube

0.43 × 0.43 × 0.43 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

T_{min} = 0.868, *T_{max}* = 1.000

5458 measured reflections

5275 independent reflections

4131 observed reflections [*I* > 2σ(*I*)]

R_{int} = 0.0254

θ_{max} = 24.97°

h = -19 → 19

k = 0 → 12

l = -20 → 0

3 standard reflections

frequency: 60 min

intensity decay: 2.3%

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.0319

wR (*F*²) = 0.0730

S = 1.025

5275 reflections

355 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0457*P*)² + 0.5300*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.318 e Å⁻³

Δρ_{min} = -0.319 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0092 (4)

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Sn1	0.017832 (13)	0.09671 (2)	0.256686 (11)	0.04563 (10)
Cl1	0.03274 (6)	-0.11244 (10)	0.18942 (6)	0.0672 (3)
O1	0.00610 (14)	0.2896 (2)	0.32489 (12)	0.0560 (6)
N1	0.0487 (2)	0.3269 (3)	0.47525 (15)	0.0494 (7)
N2	-0.1114 (2)	0.3199 (3)	0.42739 (14)	0.0470 (6)
C1	-0.0155 (2)	0.2050 (4)	0.1581 (2)	0.0523 (8)
C2	-0.0316 (2)	0.1452 (4)	0.0898 (2)	0.0651 (11)
C3	-0.0535 (3)	0.2167 (6)	0.0258 (2)	0.0863 (14)
C4	-0.0580 (3)	0.3471 (7)	0.0299 (3)	0.101 (2)
C5	-0.0424 (4)	0.4090 (5)	0.0971 (3)	0.104 (2)
C6	-0.0200 (3)	0.3382 (5)	0.1602 (2)	0.0798 (12)

C7	0.1413 (2)	0.1017 (4)	0.2969 (2)	0.0522 (8)
C8	0.1845 (2)	0.2154 (4)	0.2950 (2)	0.0668 (10)
C9	0.2657 (3)	0.2205 (6)	0.3195 (3)	0.0880 (15)
C10	0.3019 (3)	0.1146 (7)	0.3458 (3)	0.104 (2)
C11	0.2603 (3)	0.0001 (6)	0.3497 (3)	0.102 (2)
C12	0.1782 (2)	-0.0068 (5)	0.3243 (2)	0.0745 (11)
C13	-0.0784 (2)	0.0322 (3)	0.3281 (2)	0.0457 (7)
C14	-0.0681 (2)	0.0226 (4)	0.4056 (2)	0.0555 (9)
C15	-0.1325 (2)	-0.0066 (4)	0.4533 (2)	0.0635 (10)
C16	-0.2081 (2)	-0.0256 (4)	0.4238 (2)	0.0712 (11)
C17	-0.2203 (2)	-0.0171 (4)	0.3471 (3)	0.0751 (12)
C18	-0.1560 (2)	0.0111 (4)	0.2992 (2)	0.0629 (10)
C19	-0.0114 (2)	0.3407 (3)	0.5280 (2)	0.0430 (7)
C20	0.1245 (2)	0.3310 (3)	0.4997 (2)	0.0591 (9)
C21	0.1490 (2)	0.3482 (4)	0.5747 (2)	0.0585 (9)
C22	0.0892 (2)	0.3596 (3)	0.6288 (2)	0.0597 (9)
C23	0.0063 (2)	0.3574 (3)	0.6048 (2)	0.0513 (8)
C24	-0.0601 (3)	0.3738 (4)	0.6562 (2)	0.0650 (10)
C25	-0.1384 (2)	0.3718 (4)	0.6329 (2)	0.0642 (10)
C26	-0.1594 (2)	0.3517 (3)	0.5554 (2)	0.0492 (8)
C27	-0.2411 (2)	0.3447 (4)	0.5295 (2)	0.0580 (9)
C28	-0.2559 (2)	0.3193 (4)	0.4542 (2)	0.0578 (9)
C29	-0.1885 (2)	0.3107 (3)	0.4065 (2)	0.0540 (8)
C30	-0.0954 (2)	0.3376 (3)	0.5025 (2)	0.0432 (7)
C31	0.2394 (2)	0.3515 (4)	0.5924 (3)	0.0835 (13)
C32	0.1098 (3)	0.3747 (5)	0.7116 (2)	0.0898 (14)
C33	-0.3120 (3)	0.3665 (6)	0.5837 (3)	0.102 (2)
C34	-0.3398 (2)	0.3031 (5)	0.4203 (3)	0.0885 (14)

Table 2. Selected geometric parameters (Å, °)

Sn1—C1	2.142 (3)	Sn1—O1	2.348 (2)
Sn1—C7	2.142 (3)	Sn1—Cl1	2.4908 (10)
Sn1—C13	2.127 (3)		
C1—Sn1—C7	119.66 (12)	C7—Sn1—Cl1	94.91 (10)
C1—Sn1—C13	117.32 (12)	C13—Sn1—O1	84.56 (10)
C1—Sn1—O1	86.85 (12)	C13—Sn1—Cl1	94.56 (9)
C1—Sn1—Cl1	95.63 (11)	O1—Sn1—Cl1	177.49 (6)
C7—Sn1—C13	120.74 (12)	Sn1—O1···N2	120.59 (11)
C7—Sn1—O1	83.55 (11)	Sn1—O1···N1	126.14 (12)

C-bound H atoms were generated and were allowed to ride on their parent atoms with temperature factors 1.5 times those of the C atoms; the water H atoms were located and refined isotropically.

Data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 VAX/PC*. Data reduction: *Xtal3.0* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexacarbonyl($\eta^{5:1}$ -2-cyclopentadienediylethyl)(μ - $\eta^{1:3}$ -1-ethoxy-2-propenylidene)-molybdenumtungsten

WALTER FRANK, CORNELIUS G. KREITER, GUIDO J. REIß AND SABINE SCHUFFT

Fachbereich Chemie, Universität Kaiserslautern, Erwin Schrödinger-Straße, 67663 Kaiserslautern, Germany

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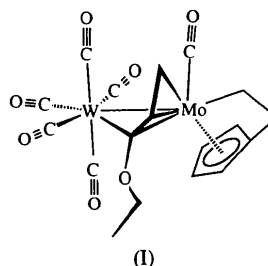
Abstract

The crystal structure of the title compound [alternative nomenclature: hexacarbonyl-1 κ^5 C, 2 κ C-2(η^5)-2-cyclopentadienediylethyl-2 κ C¹- μ -2(η^2)-1-ethoxy-2-propenylidene-1:2 κ^2 C¹-2-molybdenum-1-tungsten(Mo—W)], [(C₅H₄C₂H₄)(CO)Mo(C₃H₃OC₂H₅)W(CO)₅], (I), has been determined from single-crystal X-ray diffraction data. Geometry and bond lengths of (I) are in accord with its description as a 1-molybdena-5-tungstenatri-cyclo[2.1.0.0^{1,3}]pentane or, even better, as an *arachno*-pentagonal bipyramid with an Mo atom at the apex.

Comment

Transition metal complexes with α,β -unsaturated carbene or propenylidene ligands coordinate to 14-electron complex fragments, *e.g.* tetracarbonyl tungsten or tricarbonyl iron, in a comparable fashion to 1,3-butadiene. In the resulting dinuclear complexes the $\eta^{1:3}$ -propenylidene ligands are in bridging positions (Parlier, Rose, Rudler & Rudler, 1982; Parlier, Rudler, Rudler & Daran, 1987; Macomber, Liang & Rogers, 1988; Macomber, Liang, Madhukar & Verma, 1989; Alvarez-Toledano *et al.*, 1987).

Tricarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)molybdenum (Eilbracht, 1976) was shown to form photochemically stable η^2 - and η^4 -diene complexes with conjugated dienes (Kreiter, Michels & Wenz, 1986; Kreiter, Wenz & Bell, 1990) and is, therefore, a promising candidate for the coordination of propenylidene complexes. As pentacarbonyl(1-ethoxy-2-propenylidene)tungsten, (II) (Macomber *et al.*, 1989), is decomposed photochemically, tricarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)molybdenum, (III), was first irradiated in THF in order to obtain the reactive compound dicarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)-(tetrahydrofuran)molybdenum, which reacts readily with the title compound, (I), primarily to give orange heptacarbonyl($\eta^{1:5}$ -2-cyclopentadienediylethyl)(μ -2,3- η -1-ethoxy-2-propenylidene)molybdenum-tungsten, (IV). Even at 248 K (IV) loses carbon monoxide, forming the green title compound, (I) (Schufft, 1992).



Crystals of (I) contain discrete dinuclear complexes. The Mo atom with its carbonyl and its $\eta^{5:1}$ -chelating cyclopentadienediylethyl ligand is connected to a tungsten pentacarbonyl fragment by an Mo—W bond and the propenylidene part of the ethoxypropenylidene ligand. The Mo—W distance corresponds well with known Mo—W single bonds (Delgado, Garcia, Jeffery, Sherwood & Stone, 1988).

The propenylidene unit C1—C3, with essentially equal C—C bond lengths [C1—C2 1.396 (7) and C2—C3 1.399 (7) Å], is η^3 -coordinated to Mo and η^1 -coordinated to W. The corresponding Mo—C distances are somewhat shorter than those found for the allyl ligand in (η^3 -allyl)dicarbonyl(η^5 -cyclopentadienyl)molybdenum (Faller, Chodosh & Katahira, 1980) or for the butadiene ligand in (η^4 -1,3-butadiene)-carbonylmethyl(η^5 -pentamethylcyclopentadienyl)molybdenum, (V) (Kreiter, Wendt & Sheldrick, 1987), whereas the Mo—C17 single bond [2.313 (7) Å] is significantly longer than the Mo—methyl carbon distance [2.24 (2) Å] in (V). The coordination sphere of tungsten is distorted pentagonal bipyramidal or distorted octahedral if Mo and C(1) together are considered to occupy one coordination site. In comparison with the corresponding W—alkyl group bond in [(CO)₅WCH(OCH₃)(C₆H₅)][−] (2.34 (1) Å; Casey, Polichnowski, Tuinstra, Albin & Calabrese, 1978), the W—C1 bond is considerably shorter [2.282 (6) Å].