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(η5-Cyclopentadienyl)oxo(peroxo-O,O')-(trimethylsilylmethyl)tungsten and the Related (η5-Pentamethylcyclopentadienyl)-oxo(peroxo-O,O')(trimethylsilylmethyl)-tungsten–Tetracyanoethylene (2/1) Complex

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Abstract

The two organometallic molecules, [WO(C5H5)(C4H11-Si)(O2)] and [WO(C10H15)(C4H11Si)(O2)] [2:1 complex with C6N4 (TCNE, ethenetetracarbonitrile)], have similar piano-stool structures and separate oxo and peroxo ligands [W—O(oxo) = 1.69 (3) and 1.727 (7), W—O(peroxo) = 1.91 (mean), O—O = 1.43 (3) and 1.426 (11) Å]. The 2:1 complex contains a TCNE molecule disordered over two sites, sandwiched between two organometallic molecules, with O(peroxo)···C(TCNE) distances of 2.94(2)–3.33 (2) Å (the asymmetric unit is one Cp*W molecule and half of a TCNE molecule disordered over two sites).

Comment

The organometallic complex molecules [CpW(O)-(O2)(CH2SiMe3)], (1), where Cp is C5H5, and [Cp*W(O)(O2)(CH2SiMe3)], where Cp* is Me5C5 and which forms the 2:1 complex, (2), with TCNE, have very similar structures (see Fig. 1) and dimensions
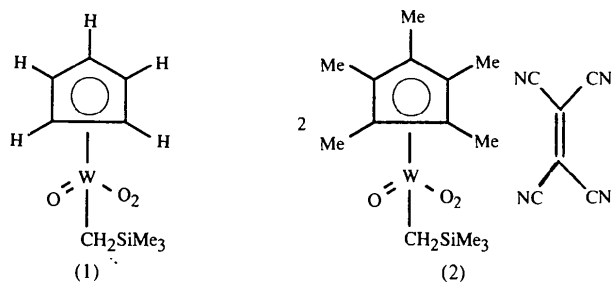
(Table 2); the dimensions are also similar in the uncomplexed Cp* compound, except for possible oxo/peroxo disorder (Faller & Ma, 1988). Both have piano-stool structures, with separate oxo and peroxo ligands. The W—O(oxo) bond distances [1.69 (3) and 1.727 (7) Å for (1) and (2), respectively] correspond to double bonds, while the W—O(peroxo) lengths [1.87 (3) and 1.92 (3) Å for (1) and 1.896 (8) and 1.931 (7) Å for (2)] are characteristic for single bonds (Allen et al., 1989). The O—O(peroxo) bond distances [1.43 (3) for (1) and 1.426 (11) Å for (2)] are close to normal single-bond lengths, and the peroxo ligands are symmetrically bonded to W. The dimensions of the alkyl ligands are normal (Allen et al., 1987, 1989): W—CH2 = 2.14 (4) and 2.156 (11), CH2—Si = 1.85 (4) and 1.849 (11), Si—Me = 1.81 (4)–1.88 (4) and 1.83 (2)–1.87 (2) Å for (1) and (2), respectively; the W—CH2—Si angles are somewhat enlarged [119 (2) and 117.6 (6)°], probably as a result of steric interactions between the methyl groups and oxo ligands. The Cp ligand dimensions are rather inaccurately determined as a result of the high thermal motion (or possible disorder). The rings are approximately planar. In (1), deviations from the mean ring plane range from 0.02 (6) for C2 to 0.11 (5) Å for C4. In (2), deviations of the ring atoms from their mean plane range from 0.002 (9) for C4 to 0.017 (9) Å for C2; the
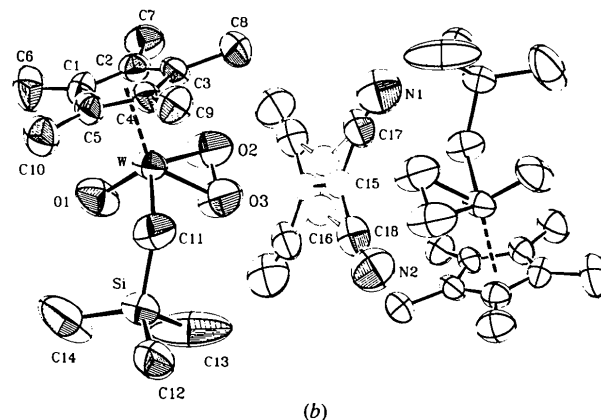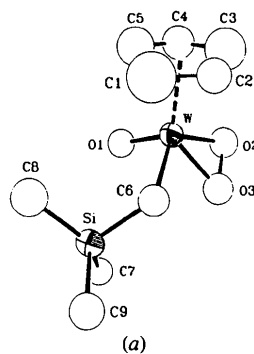
(a)

(b)

Fig. 1. Views of the molecular structures of (a) (1) and (b) (2), with 50% probability ellipsoids.

H H H H H H O≈W²O2 CH2SiMe3 (1)

Me Me Me Me Me Me O≈W²O2 CH2SiMe3 (2) NC CN NC CN 2

Me groups are displaced from the ring plane away from the W atom by amounts ranging from 0.028 (13) for C7 to 0.155 (11) Å for C9. All these dimensions are close to those in related (trimethylsilylmethyl)tungsten complexes (Legzdins, Rettig & Sánchez, 1985; Legzdins, Phillips, Rettig, Sánchez, Trotter & Yee, 1988). Since the TCNE molecule in (2) is disordered over two orientations, the dimensions are not accurately determined, but they are not far from normal values (Masnovi, Kochi, Hilinski & Rentzepis, 1985; Blackstock & Kochi, 1987) (Table 2).

The crystal structure of the 2:1 complex (2) contains an approximately planar TCNE molecule lying on an inversion centre and sandwiched between two organometallic molecules (the asymmetric unit consists of one complete organometallic molecule and one half of a TCNE molecule). In addition, the TCNE molecule is disordered in two orientations related by a 90° rotation about the normal to the molecular plane. The most significant contacts between molecules involve the O atoms of the peroxo ligand and the ethylenic C atoms of the TCNE molecule, with O$\cdots$C distances in the range 2.94 (2)–3.33 (2) Å (Table 2). Views of these contacts (Fig. 2) indicate that the peroxo groups are situated immediately above and below the C=C bond; this situation probably involves a charge-transfer interaction between the lone-pair electrons of the peroxo O atoms in the organometallic donor and the π^* orbitals of the TCNE acceptor.

Comparison may be made with the 2:1 complex of diazabicyclooctane and TCNE (Blackstock & Kochi, 1987), in which the azo (N=N) groups are situated above and below the C=C bond of TCNE; in that complex, the N=N groups are collinear with the C=C bond, but with the azo chromophore displaced from a vertical position. In the complex (2), the peroxo O—O bond is oblique with respect to the C=C bond (in both disordered orientations).

Experimental

The complexes were prepared as described by Phillips (1989) and Legzdins, Phillips, Rettig, Sánchez, Trotter & Yee (1988).

Complex (1)

Crystal data

[WO(C₅H₅)(C₄H₁₁Si)(O₂)]	Mo $K\alpha$ radiation
$M_r = 384.16$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
$Pbca$	reflections
$a = 6.531$ (6) Å	$\theta = 12$–16°
$b = 11.659$ (2) Å	$\mu = 9.7$ mm^{-1}
$c = 32.198$ (7) Å	$T = 294$ K
$V = 2452$ (3) Å³	Plate
$Z = 8$	0.45 × 0.38 × 0.15 mm
$D_x = 2.08$ Mg m^{-3}	Colourless

Data collection

Enraf–Nonius CAD-4F	$\theta_{max} = 22°$
diffractometer	$h = 0 \rightarrow 6$
ω–2θ scans	$k = 0 \rightarrow 12$
Absorption correction:	$l = 0 \rightarrow 34$
analytical	3 standard reflections
$T_{min} = 0.03$, $T_{max} = 0.24$	monitored every 150
1010 measured reflections	reflections
1010 independent reflections	intensity decay: 64%
756 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.12$
$R = 0.084$	$\Delta\rho_{max} = 3.2$ e Å^{-3}
$wR = 0.114$	(2 Å from W)
$S = 4.1$	$\Delta\rho_{min} = -1.5$ e Å^{-3}
756 reflections	Extinction correction: none
67 parameters	Atomic scattering factors
H-atom parameters not	from *International Tables*
refined (idealized sites)	*for X-ray Crystallography*
$w = 1/\sigma^2(F)$	(1974, Vol. IV)

Complex (2)

Crystal data

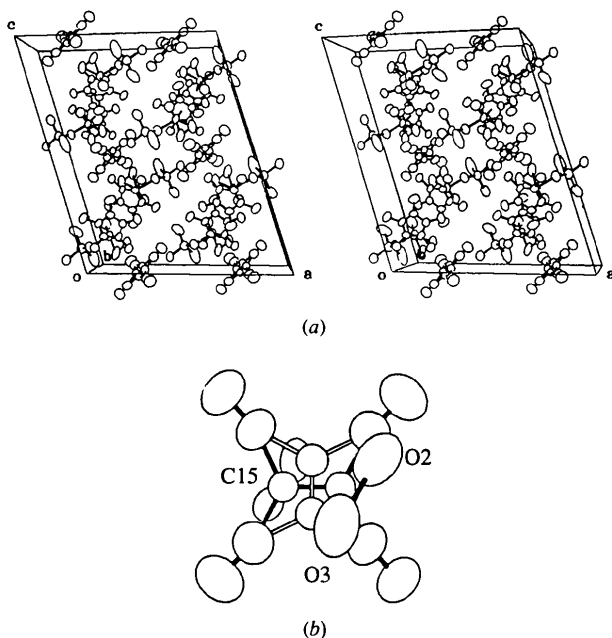|	
2[WO(C₁₀H₁₅)(C₄H₁₁Si)-	Mo $K\alpha$ radiation
(O₂)].C₆N₄	$\lambda = 0.7107$ Å
$M_r = 1036.68$	Cell parameters from 25
Monoclinic	reflections
$C2/c$	$\theta = 12$–17°
$a = 19.326$ (2) Å	$\mu = 5.6$ mm^{-1}
$b = 9.831$ (1) Å	$T = 294$ K
$c = 23.485$ (6) Å	Needle
$\beta = 107.25$ (1)°	0.44 × 0.11 × 0.09 mm

(a)

(b)

Fig. 2. (a) Stereoview of the packing of compound (2) and (b) view of the peroxo–TCNE interaction in compound (2).

$V = 4261$ (2) Å^3 Orange

$Z = 4$

$D_x = 1.62$ Mg m^{-3}

Data collection

Enraf–Nonius CAD-4F diffractometer	$\theta_{max} = 25°$
ω–2θ scans	$h = -18 \rightarrow 18$
Absorption correction: analytical	$k = 0 \rightarrow 11$
$T_{min} = 0.45$, $T_{max} = 0.67$	$l = 0 \rightarrow 22$
3731 measured reflections	3 standard reflections monitored every 150 reflections
3731 independent reflections	intensity decay: 26%
2292 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.03$
$R = 0.040$	$\Delta\rho_{max} = 1.9$ e Å^{-3}
$wR = 0.051$	(1 Å from W)
$S = 1.65$	$\Delta\rho_{min} = -2.1$ e Å^{-3}
2292 reflections	Extinction correction: none
216 parameters	Atomic scattering factors
H-atom parameters not refined (idealized sites)	from *International Tables for X-ray Crystallography*
$w = 1/\sigma^2(F)$	(1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Compound (1)				
W	0.1027 (3)	0.1164 (1)	0.0795 (1)	0.042 (2)
Si	0.0969 (23)	−0.0175 (7)	0.1745 (3)	0.039 (10)
O1	0.249 (5)	0.192 (2)	0.113 (1)	0.053 (7)†
O2	0.298 (5)	0.092 (2)	0.036 (1)	0.061 (7)†
O3	0.262 (6)	−0.007 (2)	0.061 (1)	0.064 (8)†
C1	−0.240 (15)	0.159 (5)	0.086 (2)	0.144 (25)†
C2	−0.220 (9)	0.107 (3)	0.044 (1)	0.072 (13)†
C3	−0.129 (9)	0.176 (4)	0.020 (2)	0.109 (18)†
C4	−0.051 (8)	0.265 (3)	0.044 (1)	0.071 (13)†
C5	−0.148 (9)	0.269 (4)	0.080 (2)	0.090 (16)†
C6	0.007 (8)	−0.019 (3)	0.120 (1)	0.058 (11)†
C7	0.374 (8)	−0.024 (3)	0.174 (1)	0.049 (10)†
C8	−0.001 (10)	0.108 (3)	0.201 (2)	0.084 (15)†
C9	0.008 (8)	−0.155 (3)	0.199 (1)	0.067 (13)†
Compound (2)				
W	0.33903 (2)	0.57623 (4)	0.34714 (2)	0.0607 (3)
Si	0.51000 (16)	0.7076 (4)	0.40434 (15)	0.080 (2)
O1	0.3499 (4)	0.6998 (8)	0.2982 (4)	0.097 (6)
O2	0.2673 (4)	0.6451 (10)	0.3821 (4)	0.114 (7)
O3	0.3396 (4)	0.6570 (11)	0.4206 (4)	0.129 (8)
C1	0.2916 (5)	0.4447 (9)	0.2579 (4)	0.057 (6)
C2	0.2426 (5)	0.4410 (9)	0.2927 (4)	0.056 (6)
C3	0.2758 (5)	0.3647 (10)	0.3456 (4)	0.053 (6)
C4	0.3451 (5)	0.3292 (9)	0.3435 (4)	0.054 (6)
C5	0.3551 (5)	0.3784 (10)	0.2906 (4)	0.054 (6)
C6	0.2751 (8)	0.5044 (15)	0.1981 (5)	0.097 (10)
C7	0.1675 (5)	0.4957 (13)	0.2756 (5)	0.079 (8)
C8	0.2412 (5)	0.3307 (12)	0.3932 (5)	0.073 (7)
C9	0.3968 (5)	0.2362 (11)	0.3878 (4)	0.071 (7)
C10	0.4197 (6)	0.3560 (12)	0.2697 (5)	0.079 (8)
C11	0.4526 (6)	0.5537 (11)	0.3942 (5)	0.082 (8)
C12	0.6017 (6)	0.6539 (15)	0.4514 (5)	0.095 (9)
C13	0.4769 (8)	0.8413 (14)	0.4445 (11)	0.19 (2)
C14	0.5201 (8)	0.767 (3)	0.3336 (7)	0.21 (2)
C15‡	0.264 (1)	0.296 (2)	0.021 (1)	0.049 (5)†
C16‡	0.278 (1)	0.216 (2)	0.009 (1)	0.058 (5)†
C17	0.2185 (7)	0.4135 (12)	0.0216 (5)	0.078 (8)
C18	0.3362 (7)	0.2722 (13)	0.0600 (5)	0.085 (9)
N1	0.1985 (7)	0.5153 (13)	0.0315 (5)	0.114 (9)
N2	0.3892 (6)	0.2794 (15)	0.0967 (5)	0.122 (10)

† U_{iso}.

‡ Occupancy = 0.5.

Table 2. Selected interatomic distances (Å), intermolecular contacts (Å) and angles (°)

	Compound (1)	Compound (2)
W—O(oxo)	1.69 (3)	1.727 (7)
W—O(peroxo)	1.87 (3), 1.92 (3)	1.896 (8), 1.931 (7)
W—C(Cp)	2.30 (9)–2.54 (6)	2.34 (1)–2.43 (1)
W—Cp(centroid)	2.09 (3)	2.081 (4)
W—CH2	2.14 (4)	2.156 (11)
O—O(peroxo)	1.43 (3)	1.426 (11)
CH2—Si	1.85 (4)	1.849 (11)
Si—Me	1.81 (4)–1.88 (4)	1.83 (2)–1.87 (2)
O—W—O(peroxo)	44 (1)	43.8 (3)
W—CH2—Si	119 (2)	117.6 (6)
	TCNE^a	
C=C	1.34	1.32 (4), 1.22 (4)
C—CN	1.44	1.45 (3)–1.49 (3)
C—N	1.15	1.12 (1), 1.13 (1)
C=C—C	121	116 (3)–118 (3)
C—C—N	179	160 (2)–164 (2)^b

Intermolecular contacts in (2) (peroxo· · ·ethylene)

O2· · ·C15^i	2.94 (2)	O3· · ·C15^i	3.08 (2)
O2· · ·C16^i	3.03 (3)	O3· · ·C16^i	3.24 (3)
O2· · ·C15^{ii}	3.33 (2)	O3· · ·C15^{ii}	3.15 (2)
O2· · ·C16^{ii}	3.23 (3)	O3· · ·C16^{ii}	2.96 (3)

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

Notes: (a) Masnovi, Kochi, Hilinski & Rentzepis (1985); (b) apparent deviations from 180° result from deficiency in the disordered model for the cyano C atoms.

The crystal of (1) showed extensive decomposition during the 19 h of data collection, with three standard intensities falling exponentially by an average of 75% of their initial values and the crystal changing from colourless to yellow. The data set was truncated to include only reflections measured during the first 12 h of X-ray exposure (average decay = 64%) and the data were scaled to allow for crystal decomposition. Standard reflections for (2) showed an average intensity decrease of 26% and the data were scaled accordingly.

The structures were determined by Patterson methods. The high R value for (1) probably results from poor data as a result of crystal decomposition. Peaks of residual electron density (2.5 and 3.2 e Å^{-3}) were located about 2 Å from W, but did not correspond to any disorder of the oxo/peroxo ligands. The unit cell of (2) contains eight molecules of $[Cp^*W(O)(O_2)(CH_2SiMe_3)]$ in general positions and four TCNE molecules occupying inversion symmetry centres. In addition, the TCNE molecules are disordered in two orientations rotated 90° from each other about the normal to the molecular plane. This disorder was modelled by taking two sites (occupancies = 0.5) for the ethylenic C atom; one site was assigned to each C and N atom of the cyano groups, although these atoms doubtless could be split into two closely spaced sites. Anisotropic displacement parameters were used for all non-H atoms, except the (half-weight) ethylenic C atoms.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: local program; program(s) used to refine structures: *ORFLS* (Busing, Martin & Levy, 1962); molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Trigonal Prismatic Cluster Compound of Tin and Lithium: Structure of [{Sn(OCMe2C6H4)2}3Li2O].2HOCMe2Ph

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Abstract

The structure of the title compound, μ_3-oxo-2:3:4$\kappa^3 O$-hexakis[μ-2-phenyl-2-propanolato(2−)]-1:2$\kappa^2 O$,2$\kappa C^{2'}$;-1:3$\kappa^2 O$,3$\kappa C^{2'}$;1:4$\kappa^2 O$,4$\kappa C^{2'}$;2$\kappa C^{2'}$,2:5$\kappa^2 O$;3$\kappa C^{2'}$,3:5$\kappa^2 O$;-

4$\kappa C^{2'}$,4:5$\kappa^2 O$-dilithiumtritin bis(2-phenyl-2-propanol), contains a prismatic cluster of three [Sn(OCMe2C6H4)2] units held together by one equivalent of Li2O through Sn—O—Sn and O—Li—O bridges. A central triangular Sn3O unit is sandwiched by two capping O3Li units. The Sn—O(oxo) distances are 2.100(2) and 2.088(4) Å, while the Li—O(oxo) distances are 2.342(9) Å. A crystallographic twofold axis passes through a unique Sn atom and the central oxo group of the cluster.

Comment

Recent work by our group has shown that Sn^{IV} metal centers have the ability to intramolecularly activate the aromatic C—H bonds of certain specific types of aryl-substituted alkoxide and aryloxide ligation (Smith, Visciglio, Fanwick & Rothwell, 1992). The reaction generates a series of five- and six-membered oxametalacyclic ring compounds of tin. During one of our studies of the thermal reactivity of the tetraalkoxy derivative of tin [Sn(OCMe2Ph)4], we noticed the formation of a few crystals of a material that was completely insoluble in most organic solvents. A view of this compound, (I), is shown in Fig. 1.

2HOCMe2Ph

(I)
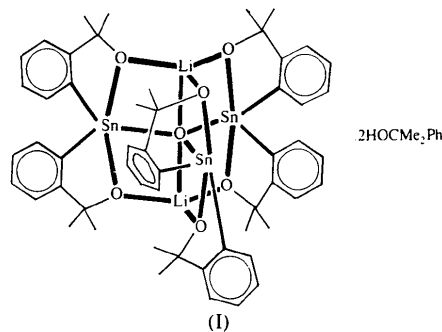
The thermolysis of the liquid tetraalkoxide [Sn(OC3Me2Ph)4] typically leads to the dinuclear compound [Sn(OCMe2C6H4)2]2 along with eliminated 2-phenylpropan-2-ol (Smith, Visciglio, Fanwick & Rothwell, 1992). The compound analyzed in this report contains three formally neutral Sn^{IV} units, [Sn(OCMe2C6H4)2], containing two five-membered metalacycles formed by cyclometalation of the *ortho*-CH bond of each of the 2-phenyl-2-propanolato groups. The three tin-containing units are held together by one equivalent of Li2O. The origin of the lithium oxide presumably stems from water contamination in the initial synthesis of the precursor [Sn(NMe2)4], obtained from SnCl4 and LiNMe2. A twofold axis of symmetry is present and passes through unique Sn(2) and O(B). Two molecules of 2-phenylpropan-2-ol per cluster unit are also present but are omitted from the *ORTEP* (Johnson, 1965) view for clarity.