Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

[{Cp$_2$(^{t}BuSe)Nb}$_2$*E*] (*E* = O and Se) with bridging oxide or selenide ligands

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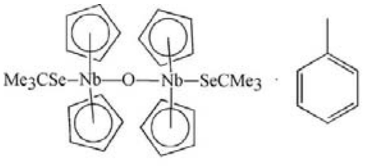
Received 14 July 2008
Accepted 4 August 2008
Online 20 September 2008

The title compounds, μ-oxido-bis[(*tert*-butylselenolato)bis(η^5-cyclopentadienyl)niobium(IV)] toluene solvate, [$Nb_2(C_5H_5)_4(C_4H_9Se)_2O$]·$C_7H_8$, and μ-selenido-bis[(*tert*-butylselenolato)bis(η^5-cyclopentadienyl)niobium(IV)], [$Nb_2(C_5H_5)_4(C_4H_9Se)_2Se$], consist of niobium(IV) centres each bonded to two η^5-coordinated cyclopentadienyl groups and one *tert*-butylselenolate ligand and are the first organometallic niobium selenolates to be structurally characterized. A bridging oxide or selenide completes the niobium coordination spheres of the discrete dinuclear molecules. In the oxide, the O atom lies on an inversion centre, resulting in a linear Nb—O—Nb linkage, whereas the selenide has a bent bridging group [Nb—Se—Nb = 139.76 (2)°]. The difference is attributable to strong π bonding in the oxide case, although the effects on the Nb—C and Nb—Se^{t}Bu bond lengths are small.

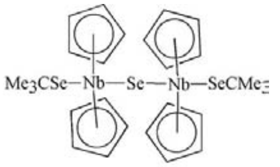
Comment

Thiolate ligands (RS^-) form complexes with most metals and metalloids. Much less is known about the corresponding compounds with the heavier chalcogens, *i.e.* the selenolates (RSe^-) and tellurolates (RTe^-) (Arnold, 1995). Current interest in selenolates derives from the observation that they can be useful precursors in the synthesis of metal selenide materials by chemical vapour deposition (CVD). The early transition metal diselenides adopt layered CdI_2-type structures with various stacking sequences and are potential sensor and photovoltaic materials, as well as being useful solid lubricants. $NbSe_2$ is a low-dimensional superconductor (Frindt, 1972) and has previously been deposited under CVD conditions from $NbCl_5$ and $^tBu_2Se$ (Boscher *et al.*, 2006). [(η^5-Cp)$_2$*M*(Se^{t}Bu)$_2$] complexes (Cp is cyclopentadienyl; *M* = Ti, Zr or Hf) were recently shown to deposit MSe_2 films by CVD (Hector *et al.*, 2008). The title compounds, (I) and (II), were derived from attempts to crystallize the very air-sensitive [(η^5-Cp)$_2$Nb(Se^{t}Bu)$_2$] complex for use in the CVD of $NbSe_2$.

Only two niobium selenolates have been structurally characterized to date. These are the [$Se_3Nb(Se^tBu)$]$^{2-}$ anion (Lorenz & Fenske, 2001) and a copper–niobium cluster, [{$Et_3PCu(\mu$-SePh)$_3$}$_2$Nb] (Feuerhake & Fenske, 2003). [(η^5-Cp)$_2$Nb(SePh)$_2$] (Sato & Yoshida, 1975) and Nb(SePh)$_3$ (Andrä, 1970) have also been reported, but without structural characterization.



(I)



(II)

Blue crystals of the title compounds were isolated from solutions of [(η^5-Cp)$_2$Nb(Se^{t}Bu)$_2$], presumably as minor by-product phases due to hydrolysis by trace water or condensation of two of the selenolate groups with elimination of $^tBu_2Se$. Crystals of [{(η^5-Cp)$_2$(Se^{t}Bu)Nb}$_2$(μ-O)]·C_7H_8, (I), are needle-shaped (blocks cut from these needles were used for crystallographic analysis), whereas those of [{(η^5-Cp)$_2$(Se^{t}Bu)Nb}$_2$(μ-Se)], (II), are blocks. The discrete molecules are dinuclear, with oxide or selenide bridges between the two Nb atoms. The remainder of the Nb coordination environment

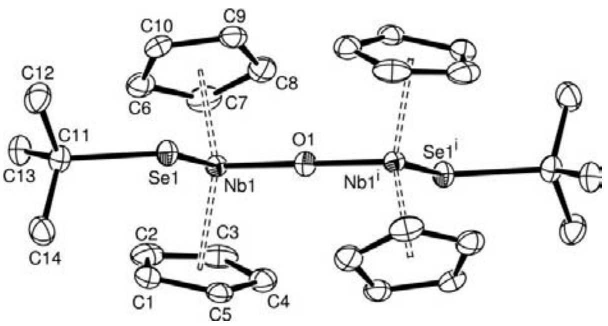


Figure 1
The discrete centrosymmetric molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and both the toluene solvent molecule and H atoms have been omitted for clarity. [Symmetry code: (i) $2 - x, -y, 2 - z$.]

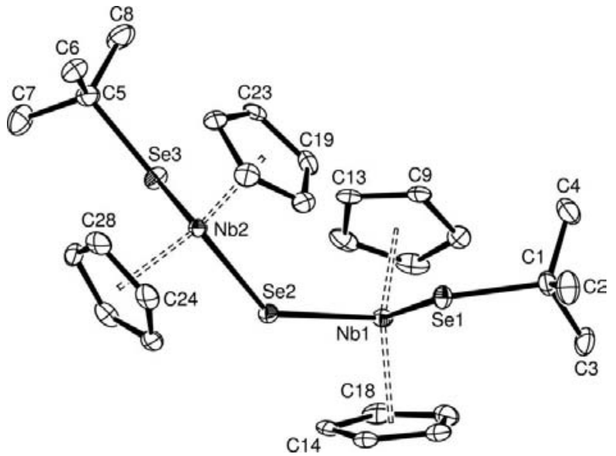


Figure 2
The discrete molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

doi:10.1107/S0108270108025055

shows a typical metallocene geometry, with each Nb atom having two η^5-coordinated Cp rings and one *tert*-butylselenolate group. The Nb—C distances are in the range 2.403 (2)–2.487 (2) Å in (I) and 2.387 (5)–2.477 (4) Å in (II). The C—C distances are normal and similar to those observed in bis(η^5-Cp) selenolates of zirconium and hafnium (Hector *et al.*, 2008).

The most striking difference between the structures of (I) and (II) is the geometry of the bridging atom between the two Nb centres. The oxide in (I) forms a linear Nb—O—Nb linkage, whereas the corresponding angle in the selenide in (II) is markedly bent [139.76 (2)°]. This difference can be attributed to a high level of π(O)—Nb bonding in the oxide case that is not present with selenide (*i.e.* in simple terms the selenide has stereochemically active lone pairs). In [{(η^5-Cp)$_2$(SeMe)Zr}$_2$(μ-O)], the Zr—O—Zr angle is 173.92 (9)° (Hector *et al.*, 2008).

The selenolate Nb—Se distance in (I) [2.6307 (4) Å] is shorter than those in [{(η^5-Cp)$_2$(SeMe)Zr}$_2$(μ-O)] [2.6645 (5)/2.6689 (5) Å] by the amount expected from the difference in the ionic radii of Nb^{4+} and Zr^{4+} (0.68 and 0.72 Å, respectively; Shannon, 1976). In (II) this distance is longer [2.6630 (11)/2.6326 (11) Å], reflecting the strong π-donation from the bridging oxide. The Nb—Se—C angles of 115.38 (6)° in (I) and 115.22 (14)/117.06 (14)° in (II) are wider than those observed in [{(η^5-Cp)$_2$(SeMe)Zr}$_2$(μ-O)] [108.70 (8)/109.05 (9)°] or [(η^5-Cp)$_2$Hf(SeMe)$_2$] [105.37 (15)°], as expected due to the steric bulk of the *tert*-butyl groups, but not as wide as in [(η^5-Cp)$_2$Zr(Se^{t}Bu)$_2$] [120.7 (3)°], where two *tert*-butylselenolate groups are in close proximity.

Experimental

LiSe^{t}Bu was produced from ^{t}BuLi (6.2 ml, 1.7 *M* in pentane) and Se powder (0.556 g, 7.04 mmol) in tetrahydrofuran (30 ml) solution. It was added to a suspension of [Cp$_2$NbCl$_2$] (1.0 g, 3.52 mmol) in toluene (20 ml) and stirred for 2 h. The solvent was removed under reduced pressure and the resulting dark-blue solid was extracted with Et$_2$O and filtered through Celite. This solution was reduced to a volume of *ca* 10 ml and dark-blue crystals of (II) were isolated by decantation (yield 147 mg). Attempts to crystallize further material from the cold supernatant solutions resulted in crystals of (I).

Compound (I)

Crystal data

[Nb$_2$(C$_5$H$_5$)$_4$(C$_4$H$_9$Se)$_2$O]·C$_7$H$_8$
M_r = 826.46
Monoclinic, $P2_1/n$
a = 8.0288 (10) Å
b = 12.7685 (15) Å
c = 15.873 (2) Å
β = 92.848 (6)°
V = 1625.3 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.97 mm^{-1}
T = 120 (2) K
0.14 × 0.06 × 0.02 mm

Data collection

Bruker–Nonius 95mm CCD camera on κ-goniostat diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{\min}$ = 0.731, $T_{\max}$ = 0.940
21963 measured reflections
3729 independent reflections
3323 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.030

Table 1
Selected geometric parameters (Å, °) for (I).

Nb1—O1	1.9300 (3)	Se1—C11	2.021 (2)
Nb1—Se1	2.6307 (4)		
Nb1—O1—Nb1^i	180	C11—Se1—Nb1	115.38 (6)
O1—Nb1—Se1	79.791 (11)		

Symmetry code: (i) $-x + 2, -y, -z + 2$.

Table 2
Selected geometric parameters (Å, °) for (II).

Nb1—Se1	2.6630 (11)	Nb2—Se3	2.6326 (11)
Nb1—Se2	2.5488 (9)	Se1—C1	2.014 (5)
Nb2—Se2	2.5366 (7)	Se3—C5	2.034 (5)
Nb2—Se2—Nb1	139.76 (2)	C4—C1—Se1	111.7 (3)
Se2—Nb1—Se1	83.97 (3)	C2—C1—Se1	104.7 (3)
Se2—Nb2—Se3	84.24 (3)	C6—C5—Se3	113.6 (3)
C1—Se1—Nb1	117.06 (14)	C7—C5—Se3	106.3 (3)
C5—Se3—Nb2	115.22 (14)	C8—C5—Se3	106.2 (3)
C3—C1—Se1	111.0 (3)		

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.051
S = 1.17
3729 reflections
206 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.57 e Å^{-3}

Compound (II)

Crystal data

[Nb$_2$(C$_5$H$_5$)$_4$(C$_4$H$_9$Se)$_2$Se]
M_r = 797.28
Monoclinic, $C2/c$
a = 31.583 (8) Å
b = 7.9548 (15) Å
c = 26.520 (7) Å
β = 121.29 (2)°
V = 5694 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 4.66 mm^{-1}
T = 120 (2) K
0.12 × 0.09 × 0.06 mm

Data collection

Bruker–Nonius 95mm CCD camera on κ-goniostat diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{\min}$ = 0.514, $T_{\max}$ = 0.756
31432 measured reflections
6538 independent reflections
4694 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.075
S = 1.02
6538 reflections
298 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.79 e Å^{-3}
$\Delta\rho_{\min}$ = −0.82 e Å^{-3}

H atoms were placed in calculated positions, with C—H = 0.95 (Cp and Ph of the toluene solvent molecule) or 0.98 Å (methyl). $U_{\rm iso}$(H) values for methyl H atoms were set at 1.5$U_{\rm eq}$(C) and the rest at 1.2$U_{\rm eq}$(C). For (I), the disordered toluene solvent was modelled as two overlapping orientations related by a centre of symmetry and the AFIX 137 command in *SHELXL97* (Sheldrick, 2008) was used to determine the orientation of the H atoms of the methyl group.

For both compounds, data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*;

program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the EPSRC (grant No. EP/C001176/1) and the Royal Society (University Research fellowship to ALH) for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3060). Services for accessing these data are described at the back of the journal.

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