

$[\text{Cl}_5\text{Ta}(\mu\text{-O})\text{TaCl}_3\{\text{}^i\text{PrS}(\text{CH}_2)_2\text{S}^i\text{Pr}\}]$ and $[(\text{TaCl}_4)_2(\mu\text{-O})(\mu\text{-Me}_2\text{Se}_2)]$: two chalcogenoether complexes of Ta_2OCl_8 with very different geometries

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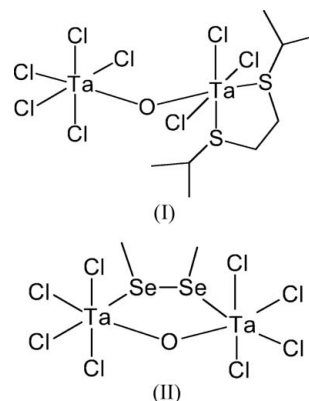
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The title compounds, [1,2-bis(isopropylsulfanyl)ethane- $2\kappa^2\text{S},\text{S}'$]octachlorido- $1\kappa^5\text{Cl},2\kappa^3\text{Cl}-\mu$ -oxido-ditantalum(V), $[\text{Ta}_2\text{Cl}_8\text{O}(\text{C}_8\text{H}_{18}\text{S}_2)]$, (I), and μ -dimethyldiselane- $\kappa^2\text{Se}:\text{Se}'-\mu$ -oxido-bis[tetrachloridotantalum(V)], $[\text{Ta}_2\text{Cl}_8\text{O}(\text{C}_2\text{H}_6\text{Se}_2)]$, (II), contain six-coordinate Ta^{V} centres linked by a nonlinear oxide bridge. Compound (I) contains one Ta^{V} centre bonded to a chelating dithioether and three terminal chloride ligands, with the second Ta^{V} centre bonded to five terminal chloride ligands. In (II), two tetrachloridotantalum(V) residues are bridged by the diselenide, giving a puckered five-membered Ta/O/Ta/Se/Se ring. The Ta—O distances in the bridges are short in both compounds, indicating that significant multiple-bond character is retained despite the deviation from linearity, and the bond lengths reveal a clear *trans* influence order of $\text{O} > \text{Cl} > \text{S} > \text{Se}$ on the hard Ta^{V} centre. The structures are compared with the $[\text{Ta}_2\text{OCl}_{10}]^{2-}$ anion, which contains a linear oxide bridge.

Comment

The centrosymmetric $[\text{Ta}_2\text{OCl}_{10}]^{2-}$ anion, often obtained by serendipitous hydrolysis in syntheses using TaCl_5 , has D_{4h} symmetry with a linear Ta—O—Ta unit and short Ta—O bonds (1.88–1.90 Å), indicative of some multiple-bonding character [$\text{O}(p\pi) \rightarrow \text{Ta}(d\pi)$; Cotton & Najjar, 1981; Noll & Mueller, 1999; Xi *et al.*, 2010]. The parent oxide–chloride, Ta_2OCl_8 , is unknown and analogues with neutral ligands have not been described hitherto. During studies of the complexes of MX_5 ($M = \text{Nb}$ or Ta ; $X = \text{F}$, Cl or Br) with chalcogenoether ligands (Benjamin *et al.*, 2011; Jura *et al.*, 2010, 2009), we obtained crystals of the title compounds, the first two examples of such complexes, *viz.* $[\text{Cl}_5\text{Ta}(\mu\text{-O})\text{TaCl}_3\{\text{}^i\text{PrS}(\text{CH}_2)_2\text{S}^i\text{Pr}\}]$, (I), and $[(\text{TaCl}_4)_2(\mu\text{-O})(\mu\text{-Me}_2\text{Se}_2)]$, (II), which show very different architectures and significant differences in bond lengths and angles. The formation of these complexes is clearly

the result of adventitious hydrolysis during attempts at crystal growth of the corresponding TaCl_5 complexes. In (I), the dithioether chelates to a TaCl_3 unit which is linked *via* the oxide bridge to a TaCl_5 unit, whilst in (II) the chalcogen ligand bridges the Ta—O—Ta unit to give a puckered five-membered ring.



The deep-yellow crystals of (I) contain a distorted square-pyramidal TaCl_5 unit about atom Ta2 (Fig. 1), with the sixth position occupied by the bridging oxide group [Ta2—O1 = 2.057 (4) Å; Table 1], whereas atom Ta1 has a more distorted octahedral geometry composed of three *mer* chloride ligands, two *cis* S atoms from a chelating dithioether and a markedly shorter bond to the bridging oxide group [Ta1—O1 = 1.787 (4) Å]. The dithioether is in the *DL* conformation (the *ⁱPr* groups are on opposite sides of the TaS_2 plane), with long Ta—S bonds (Table 1), reflecting the weak affinity of the hard Ta^{V} centre for the soft neutral S-atom donor. The bond-length distribution about the Ta centres shows clear evidence for the *trans* influence order $\text{O} > \text{Cl} > \text{S}$ on the hard Ta^{V} centre. The Ta2—O1—Ta1 bridge is nonlinear [$165.9(3)^\circ$], in contrast with that in $[\text{Ta}_2\text{OCl}_{10}]^{2-}$.

The deep-orange crystals of (II) also contain a nonlinear [$164.26(15)^\circ$] oxide bridge, with Ta1—O1 = 1.874 (2) Å and Ta2—O1 = 1.917 (2) Å (Fig. 2 and Table 2), linking two distorted octahedral Ta^{V} centres. The diselane ligand bridges

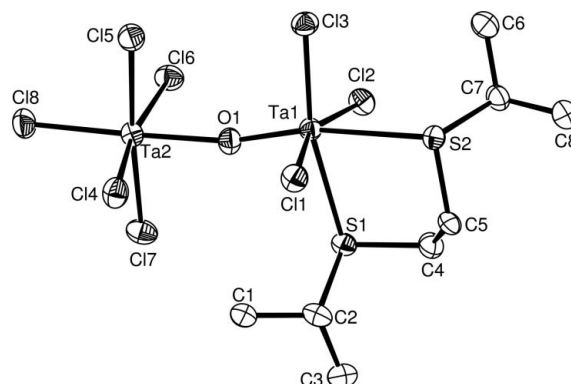


Figure 1
The discrete molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

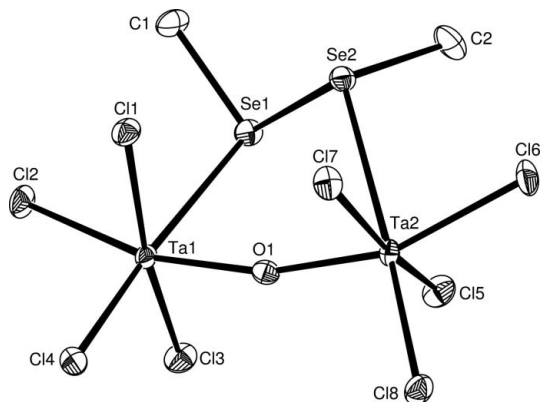


Figure 2
The discrete molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

the Ta—O—Ta unit [Ta1—Se1 = 2.8715 (4) Å and Ta2—Se2 = 2.8701 (4) Å; Table 2], forming a nonplanar five-membered ring with acute O—Ta—Se angles and much wider Ta—Se—Se angles (Table 2). The Se—Se distance is rather longer than in the gas-phase diselenide [2.326 (3) Å; D'Antonio *et al.*, 1971]. Notably, the Ta—O—Ta angles in both (I) and (II) differ by less than 2°, suggesting that the constraints of the ring in (II) are not responsible for the deviation from linearity.

Comparison of the core geometries in (I), (II) and [Ta₂OCl₁₀]²⁻ (Cotton & Najjar, 1981) reveals that in [Ta₂OCl₁₀]²⁻ the Ta—Cl(*trans* to O) bond [2.381 (6) Å] is longer than the Ta—Cl(*trans* to Cl) bond. In (II), the corresponding trend is not clear. However, as noted above, in (I) the bridging oxide interacts more strongly with Ta1 [Ta1—O1 = 1.787 (4) Å], with greater O(*pπ*)→Ta(*dπ*) donation compensating for the presence of only three *π*-donor chlorides and weak donation from the S atoms. In contrast, for atom Ta2, which carries five *π*-donor chlorides, the Ta2—O1 bond is much longer [2.057 (4) Å], and this correlates with Ta—Cl(*trans* to O) being shorter [2.2916 (17) Å] than Ta—Cl(*trans* to Cl) [2.3166 (17)–2.3622 (17) Å]. Consideration of the patterns in the bond lengths and the *trans* influence order described above would suggest that, despite the different architectures in the three compounds, the dominant interactions are those between the electron-poor Ta^V centres and the *π*-donor oxide and chloride ligands, with the neutral chalcogenoethers weakly bound and filling available coordination sites. The strong Ta—O—Ta bonds are evident from the IR spectra of all three compounds, which show a very strong and broad feature at *ca* 800 cm⁻¹ ascribed to the anti-symmetric stretching vibration of this unit (Dehnicke & Prinz, 1982).

Experimental

For the preparation of [Cl₅Ta(*μ*-O)TaCl₃{ⁱPrS(CH₂)₂SⁱPr}], (I), [(TaCl₅)₂{*μ*-ⁱPrS(CH₂)₂SⁱPr}] (0.2 g) [prepared from TaCl₅ and ⁱPrS(CH₂)₂SⁱPr in anhydrous CH₂Cl₂] was dissolved in anhydrous CH₂Cl₂ (3 ml), *n*-hexane (2 ml) was layered on top and the mixture

refrigerated. Small yellow crystals of (I) grew after a few days, and these were isolated by decanting off the mother liquor and then dried *in vacuo*. ¹H NMR (CD₂Cl₂, 295 K): δ 1.43 (*d*, *J* = 6 Hz, 6H), 1.63 (*d*, *J* = 6 Hz, 6H), 3.29 (*m*, 2H), 3.54 (*m*, 2H), 3.62–3.69 (*m*, 2H); IR (Nujol, *ν*, cm⁻¹): 801 (*vs*, *br*) (Ta—O—Ta); 368 (*m*), 349 (*s*), 317 (*s*) (Ta—Cl).

For the preparation of [(TaCl₄)₂(*μ*-O)(*μ*-Me₂Se₂)], (II), TaCl₅ (0.36 g, 1.0 mmol) was suspended in anhydrous CH₂Cl₂ (10 ml) and stirred whilst Me₂Se₂ (0.37 g, 1.0 mmol) was slowly added. The reaction mixture rapidly turned deep orange and after 10 min was concentrated to 3 ml *in vacuo*. The orange precipitate was separated off and washed with dry hexane (10 ml). Refrigeration of the filtrate for several days gave deep-orange crystals of (II), which were manually separated from an orange oil and rinsed with *n*-hexane. ¹H NMR (CD₂Cl₂, 295 K): δ 3.15 (*s*); IR (Nujol, *ν*, cm⁻¹): 800 (*vs*) (Ta—O—Ta); 336 (*sh*), 315 (*vs*, *br*) (Ta—Cl).

Compound (I)

Crystal data

[Ta ₂ Cl ₈ O(C ₈ H ₁₈ S ₂)]	<i>V</i> = 4484.4 (14) Å ³
<i>M_r</i> = 839.84	<i>Z</i> = 8
Orthorhombic, <i>Pbca</i>	Mo <i>K</i> α radiation
<i>a</i> = 15.684 (3) Å	<i>μ</i> = 10.89 mm ⁻¹
<i>b</i> = 13.007 (2) Å	<i>T</i> = 120 K
<i>c</i> = 21.981 (4) Å	0.15 × 0.06 × 0.01 mm

Data collection

Bruker–Nonius APEXII CCD camera on <i>κ</i> -goniostat diffractometer	36044 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	5139 independent reflections
<i>T</i> _{min} = 0.425, <i>T</i> _{max} = 0.897	4364 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.055

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.036	194 parameters
<i>wR</i> (<i>F</i> ²) = 0.072	H-atom parameters constrained
<i>S</i> = 1.10	Δ <i>ρ</i> _{max} = 1.26 e Å ⁻³
5139 reflections	Δ <i>ρ</i> _{min} = -1.23 e Å ⁻³

Compound (II)

Crystal data

[Ta ₂ Cl ₈ O(C ₂ H ₆ Se ₂)]	<i>V</i> = 3271.3 (4) Å ³
<i>M_r</i> = 849.49	<i>Z</i> = 8
Monoclinic, <i>C2/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 28.447 (3) Å	<i>μ</i> = 19.10 mm ⁻¹
<i>b</i> = 8.2681 (5) Å	<i>T</i> = 120 K
<i>c</i> = 16.2051 (10) Å	0.15 × 0.10 × 0.04 mm
β = 120.875 (5)°	

Data collection

Bruker–Nonius APEXII CCD camera on <i>κ</i> -goniostat diffractometer	21221 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	3762 independent reflections
<i>T</i> _{min} = 0.219, <i>T</i> _{max} = 0.466	3585 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.035

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.018	138 parameters
<i>wR</i> (<i>F</i> ²) = 0.041	H-atom parameters constrained
<i>S</i> = 1.10	Δ <i>ρ</i> _{max} = 0.89 e Å ⁻³
3762 reflections	Δ <i>ρ</i> _{min} = -1.16 e Å ⁻³

Table 1

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

Ta1—O1	1.787 (4)	Ta2—O1	2.057 (4)
Ta1—Cl3	2.2826 (17)	Ta2—Cl8	2.2916 (17)
Ta1—Cl1	2.3177 (16)	Ta2—Cl4	2.3166 (17)
Ta1—Cl2	2.3429 (17)	Ta2—Cl7	2.3354 (17)
Ta1—S1	2.6511 (17)	Ta2—Cl5	2.3452 (17)
Ta1—S2	2.7486 (16)	Ta2—Cl6	2.3622 (17)
O1—Ta1—S1	89.74 (15)	S1—Ta1—S2	80.76 (5)
O1—Ta1—S2	168.44 (15)	Ta1—O1—Ta2	165.9 (3)

Table 2

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

Ta1—O1	1.874 (2)	Ta2—Cl8	2.2543 (9)
Ta1—Cl4	2.2632 (9)	Ta2—Cl7	2.3198 (9)
Ta1—Cl1	2.3130 (9)	Ta2—Cl6	2.3215 (9)
Ta1—Cl3	2.3483 (9)	Ta2—Cl5	2.3305 (10)
Ta1—Cl2	2.3578 (9)	Ta2—Se2	2.8701 (4)
Ta1—Se1	2.8715 (4)	Se1—Se2	2.3471 (6)
Ta2—O1	1.917 (2)		
O1—Ta1—Se1	78.18 (8)	C2—Se2—Ta2	105.35 (13)
O1—Ta2—Se2	77.46 (7)	Se1—Se2—Ta2	98.318 (16)
Cl1—Se1—Ta1	105.43 (13)	Ta1—O1—Ta2	164.26 (15)
Se2—Se1—Ta1	94.861 (16)		

H atoms were placed in calculated positions, with C—H = 0.98 (methyl) or 0.99 Å (CH₂), and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl or $1.2U_{\text{eq}}(\text{C})$ for methylene groups. The AFIX 137 command (SHELXL97; Sheldrick, 2008) was used for the methyl groups to estimate their initial conformations.

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: DIRDIF99 (Beurskens *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3411). Services for accessing these data are described at the back of the journal.

References

- Benjamin, S. L., Hyslop, A., Levason, W. & Reid, G. (2011). Unpublished work.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1999). *The DIRDIF99 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Cotton, F. A. & Najar, R. C. (1981). *Inorg. Chem.* **20**, 1866–1869.
- D'Antonio, P., George, C., Lowrey, A. H. & Karle, J. (1971). *J. Chem. Phys.* **55**, 1071–1076.
- Dehnicke, K. & Prinz, H. (1982). *Z. Anorg. Allg. Chem.* **490**, 171–174.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Jura, M., Levason, W., Ratnani, R., Reid, G. & Webster, M. (2010). *Dalton Trans.* **39**, 883–891.
- Jura, M., Levason, W., Reid, G. & Webster, M. (2009). *Dalton Trans.* pp. 7610–7612.
- Noll, A. & Mueller, U. (1999). *Z. Anorg. Allg. Chem.* **625**, 1721–1725.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2007). *SADABS*. Version 2007/2. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Xi, T., Brockner, W. & Gjikaj, M. (2010). *Z. Anorg. Allg. Chem.* **636**, 2633–2640.