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Organometallic Selenolates. IX.† (18-Crown-6)potassium (η^5 -Cyclopentadienyl)bis(1,4-tetraselenido- Se^1, Se^4 -tungstate(IV))

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Abstract

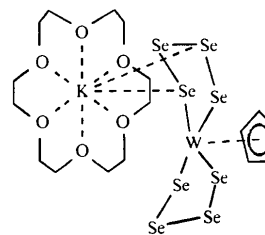
The title compound, $[(18\text{-crown-6})K]^+[W(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-Se}_4)_2]^-$ or $[K(C_{12}H_{24}O_6)][W(C_5H_5)(Se_4)_2]$, consists of the anion $[CpW(Se_4)_2]^-$ (where Cp is cyclopentadienyl), which is linked to the $[(18\text{-crown-6})K]^+$ cation via two potassium–selenium contacts of 3.457 (5) and 3.527 (5) Å. One of the WSe_4 rings adopts an envelope conformation, whereas the other WSe_4 ring lies between the standard envelope and half-chair conformations.

† Part VIII: Jones *et al.* (1998).

The corresponding W–Se bond lengths lie in the range 2.441 (2)–2.570 (2) Å, indicating asymmetry in the chelation of both Se_4 ligands, which can also be seen from the Se–Se bond-length range of 2.300 (4)–2.447 (3) Å.

Comment

Transition-metal–selenido complexes exhibit interesting structural features associated with a variety of binding modes of the Se_n^{2-} ligands. Numerous crystal structures of (oligoselenido)metallate complexes have been reported, of which $M(Se_4)_n^{2-}$ complexes are the most common (Cambridge Structural Database, Version of October 1997; Allen & Kennard, 1993; Wardle, Bhaduri *et al.*, 1988), because of the high stability of five-membered MSe_4 rings. However, examples of organometallic $RM(Se_4)_x$ systems are rare. During our studies on new syntheses of transition-metal–selenido complexes, we described the formation of the tetraselenido complex $[CpW(CO)_3]_2Se_4$ (where Cp is cyclopentadienyl) via insertion of elemental selenium into the alkali-metal–tungsten bond of $[LiW(CO)_3]$ in an appropriate ratio and subsequent oxidation with oxygen on SiO_2 (Jones & Thöne, 1996). A crystal structure analysis revealed a $\mu_2\text{-}\eta^1$ bonding pattern of the Se_4^{2-} ligand (Jones *et al.*, 1998). We present here the crystal structure of $[(18\text{-crown-6})K]^+[CpW(Se_4)_2]^-$, (1).



(1)

Compound (1) consists of a cation–anion pair. The K^+ cation lies 0.694 (8) Å out of the best plane through the O atoms of the crown ether [$K\text{—}O$ 2.774 (14)–2.939 (14) Å] and is involved in weak interionic $K\cdots Se$ contacts of 3.457 (5) ($K\cdots Se1$) and 3.527 (5) Å ($K\cdots Se3$). The $[CpW(Se_4)_2]^-$ anion consists of two WSe_4 rings with a common W atom. The coordination geometry at the W atom is slightly distorted tetragonal pyramidal, with W 0.999 (1) Å out of the basal plane (atoms Se1, Se4, Se5 and Se8; r.m.s. deviation 0.42 Å). The $Se\cdots Se$ contacts in this plane range from 2.937 (3) to 3.519 (3) Å, with $Se\cdots Se\cdots Se$ angles between 82.73 (7) and 95.52 (7)°. The W–Cp(centre) vector makes an angle of 180 (1)° with the normal to the base of the pyramid.

The chelation of the Se_4^{2-} ligands is asymmetric in both WSe_4 rings; as seen from the W–Se bond

lengths in each ring [ring A: W—Se1 2.570 (2) and W—Se4 2.441 (2) Å; ring B: W—Se5 2.529 (2) and W—Se8 2.444 (2) Å]. A comparable but less pronounced bonding asymmetry can be seen in the analogous [CpMo(Se₄)₂][−] anion, in which the shorter Mo—Se bonds are 2.463 (1) and 2.474 (1) Å, whereas the other Mo—Se bond lengths, 2.533 (1) and 2.542 (1) Å, are only slightly longer (Herath Banda *et al.*, 1989).

The W—Se bond lengths in (1) are comparable with those observed in other W_nSe_m^{2−} anions [cf. 2.395 (3)–2.546 (3) Å in (η²-Se₂)WSe(μ-Se)₂WSe(η²-Se₃) and 2.401 (3)–2.556 (3) Å in (η²-Se₂)WSe(μ-Se)₂-WSe(η²-Se₄); Wardle *et al.*, 1987]. These anions also contain W=Se double bonds with lengths 2.242 (3)–2.258 (3) Å.

The intra-chelate angles in (1) are 87.29 (8) (Se1—W—Se4) and 90.09 (8)° (Se8—W—Se5), and the inter-chelate angles are 71.67 (8) (Se8—W—Se1) and 74.33 (8)° (Se4—W—Se5). Closely similar values can be found in the [CpMo(Se₄)₂][−] anion. More symmetric chelation of the Se₄^{2−} ligand can be observed in the anions [MoO(Se₄)₂]^{2−} and [WS(Se₄)₂]^{2−}, in which the M—Se bond lengths differ only slightly, *i.e.* [MoO(Se₄)₂]^{2−} 2.465 (1)–2.512 (1) Å and [WS(Se₄)₂]^{2−} 2.435 (1)–2.487 (1) Å (Wardle, Mahler *et al.*, 1988).

The Se—Se bond lengths lie in the range 2.300 (4) (Se6—Se7) to 2.447 (3) Å (Se3—Se4). The longest bonds in this range correspond to the shorter neighbouring W—Se bonds, whereas the shortest bonds are observed between the β-Se atoms. Similar bond lengths were observed in both [MoSe(Se₄)₂]^{2−} [Se—Se 2.291 (5)–2.461 (5) Å; O'Neal & Kolis, 1988] and [CpMo(Se₄)₂]^{2−} (2.310–2.419 Å). However, in the organometallic derivative [CpW(CO)₃]₂(μ₂-η¹-Se₄), a different situation was found. The W-bonded Se₂ moieties display shorter Se—Se bond lengths [2.321 (2) and 2.322 (2) Å] than the central Se—Se bond length of 2.367 (2) Å (Jones *et al.*, 1998).

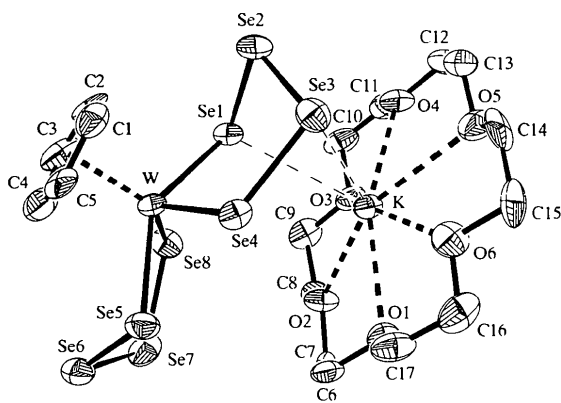


Fig. 1. The structure of (1) in the crystal. H atoms have been omitted. Ellipsoids represent 50% probability.

The WSe₄ rings in (1) display two different conformations. Ring A (W, Se1–Se4) adopts an arrangement that lies between the standard envelope and half-chair conformations. Ring B (W, Se5–Se8) adopts an envelope conformation with the flap at Se6. Essentially the same situation can be observed in the corresponding molybdenum anion. An interesting case was described for the [Pt(Se₄)₃]^{2−} ion, in which all PtSe₄ rings adopt an envelope conformation with β-Se atoms as the flaps (Ansari & Ibers, 1989). This arrangement leads to a pseudo-octahedral geometry at platinum and therefore to chirality. For the [Pt(S₅)₃]^{2−} anion, the optical isomers were resolved (Gillard & Wimmer, 1978).

Experimental

[(18-crown-6)K]⁺[CpW(Se₄)₂][−] was obtained from the reaction of K₂Se₈ with 18-crown-6 and CpW(CO)₃Cl according to Jones *et al.* (1998). Single crystals were obtained by layering a dichloromethane solution with diethyl ether.

Crystal data

[K(C₁₂H₂₄O₆)] [W(C₅H₅)(Se₄)₂]

M_r = 1184.03

Monoclinic

*P*2₁/*n*

a = 13.488 (5) Å

b = 10.113 (3) Å

c = 22.223 (10) Å

β = 98.78 (2)°

V = 2996 (2) Å³

Z = 4

D_x = 2.625 Mg m^{−3}

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 62

reflections

θ = 5.5–12.5°

μ = 13.744 mm^{−1}

T = 173 (2) K

Plate

0.42 × 0.18 × 0.02 mm

Dark green

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction:

ψ scans (*XEMP*; Siemens,

1994a) assuming lamina

100

T_{min} = 0.113, *T_{max}* = 0.760

7747 measured reflections

5238 independent reflections

2705 reflections with

I > 2σ(*I*)

R_{int} = 0.089

θ_{max} = 25.01°

h = −15 → 16

k = −12 → 4

l = −26 → 4

3 standard reflections

every 247 reflections

intensity decay: 1%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.065

wR(*F*²) = 0.164

S = 0.920

5238 reflections

298 parameters

H atoms constrained

w = 1/[σ²(*F_o*²) + (0.0721*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 2.15 e Å^{−3}

Δρ_{min} = −1.25 e Å^{−3}

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

W—Se4	2.441 (2)	Se2—Se3	2.325 (3)
W—Se8	2.444 (2)	Se3—Se4	2.447 (3)
W—Se5	2.529 (2)	Se3—K	3.527 (5)
W—Se1	2.570 (2)	Se5—Se6	2.386 (4)
Se1—Se2	2.378 (3)	Se6—Se7	2.300 (4)
Se1—K	3.457 (5)	Se7—Se8	2.442 (3)
Se4—W—Se8	124.74 (8)	Se3—Se2—Se1	96.16 (10)
Se4—W—Se5	74.33 (8)	Se2—Se3—Se4	99.45 (11)
Se8—W—Se5	90.09 (8)	Se2—Se3—K	91.32 (10)
Se4—W—Se1	87.29 (8)	Se4—Se3—K	80.92 (11)
Se8—W—Se1	71.67 (8)	W—Se4—Se3	114.03 (9)
Se5—W—Se1	140.21 (8)	Se6—Se5—W	103.89 (10)
Se2—Se1—W	101.82 (9)	Se7—Se6—Se5	96.95 (13)
Se2—Se1—K	92.16 (11)	Se6—Se7—Se8	97.73 (12)
W—Se1—K	103.66 (9)	Se7—Se8—W	114.46 (11)
Se4—W—Se1—Se2	-53.46 (10)	Se8—W—Se5—Se6	-43.48 (12)
W—Se1—Se2—Se3	65.60 (12)	W—Se5—Se6—Se7	63.12 (12)
Se1—Se2—Se3—Se4	-43.10 (13)	Se5—Se6—Se7—Se8	-48.51 (12)
Se1—W—Se4—Se3	25.73 (11)	Se6—Se7—Se8—W	23.19 (15)
Se2—Se3—Se4—W	9.73 (14)	Se5—W—Se8—Se7	12.28 (12)

H atoms were included using a riding model. The residual electron density of $2.15 \text{ e } \text{Å}^{-3}$ is 1.0 Å from the W atom, and that of $-1.25 \text{ e } \text{Å}^{-3}$ is 1.45 Å from W. This may be attributed to residual absorption errors associated with an extremely thin plate.

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994b). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1451). Services for accessing these data are described at the back of the journal.

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Bis(tetra-*n*-butylammonium) Bis[(methyl-lactato)dioxovanadate(V)] Dihydrate†

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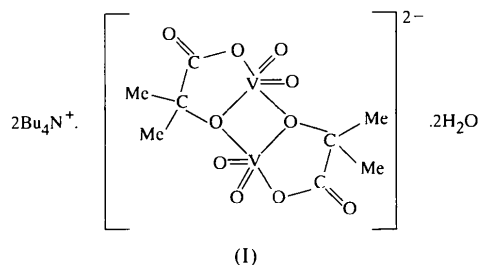
(Received 9 December 1997; accepted 25 February 1998)

Abstract

The crystal structure of $(\text{Bu}_4\text{N})_2[\text{VO}_2(\text{C}_4\text{H}_6\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$ consists of the dimeric $[\{\text{VO}_2(\text{C}_4\text{H}_6\text{O}_3)\}_2]^{2-}$ anion with C_i symmetry, two Bu_4N^+ cations and two water molecules. The V atom is pentacoordinated by O atoms in a tetragonal-pyramidal arrangement.

Comment

Knowledge of the properties of vanadate complexes is essential to vanadium biochemistry. Information about the interactions of vanadate with biogenic ligands will be needed so that the most potent and biologically significant interactions can be identified (Sigel & Sigel, 1995). In the course of our work on model oxygen-vanadium compounds (Sabirov *et al.*, 1984; Angus-Dunne *et al.*, 1994), we isolated the title compound, (I).



† Systematic name: bis(tetra-*n*-butylammonium) bis[μ -2-hydroxy-2-methylpropanoato(2-)]- $1\kappa^2 O^1, O^2:2\kappa O^2; 1\kappa O^2:2\kappa^2 O^1, O^2$ -bis[dioxovanadate(V)] dihydrate.