# Hexapotassium di-μ-dioxosulfato-bis[tetracyano-osmate(III)](*Os—Os*) dihydrate

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The title compound, $K_6[Os_2(CN)_8(SO_2)_2]\cdot 2H_2O$, was prepared from the reaction of OsO_4 with elemental Se and S_2Cl_2 at 473 K and further reaction with aqueous KCN solution. It contains a centrosymmetric binuclear $[Os_2S_2O_4(CN)_8]^{6-}$ cluster anion.

Comment

The chemistry of cyanide and chalcocyanide compounds of transition metals has been developed extensively in recent years (Gabriel *et al.*, 2001; Mironov & Fedorov, 2002; Naumov *et al.* 2000; Kalinina & Fedin, 2003). It is well known that osmium complexes can react with alkali metal cyanides, with the cyanide ligands entering the Os coordination sphere and concomitant reduction of the osmium. For example, $K_2[Os^{IV}Cl_6]$ or $K_2[Os^{VI}I_4]$ complexes react with aqueous or molten cyanides with the formation of $K_4[Os^{II}(CN)_6]$ (Livingston, 1978). Here, we report the synthesis and structure of the title compound, (I), which is the first cluster chalcocyanide of Os. It is isostructural with $K_6Re_2S_2O_4(CN)_8\cdot 2H_2O$, which contains the $[Re_2S_2O_4(CN)_8]^{6-}$ cluster anion (Muller *et al.* 1991).

(I)
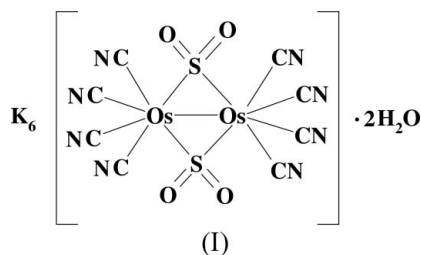
Compound (I) (Fig. 1) contains the binuclear-cluster anionic unit $[Os_2S_2O_4(CN)_8]^{6-}$. The major difference between the Os and Re compounds is the length of the metal–metal bond, with the Os—Os distance in (I) of 2.8546 (6) Å being longer than the corresponding Re—Re distance of 2.653 (1) Å in $[Re_2S_2O_4(CN)_8]^{6-}$.

The complete cluster in (I) is generated by inversion symmetry and each Os atom is coordinated by two SO_2 ligands, with Os—μ_2-S distances of 2.319 (2) and 2.321 (1) Å (Table 1). The Os atom is further coordinatd by four terminal cyano ligands, with Os—C distances in the range 2.044 (7)–2.057 (6) Å. K^+ cations and water molecules complete the structure of (I).

Experimental

OsO_4 and a 22% solution of elemental Se in S_2Cl_2 (ratio solid:liquid = 1:10) were loaded into a reactor under argon. The reaction mixture

was heated at 313–323 K with full dissolution of OsO_4 and isolation of SO_2. The temperature was then raised to 343–363 K and SO_2 was removed completely. The reactor was then sealed and placed in an oven at 473 K for 40 h. After reaction, the product was washed with S_2Cl_2, CS_2 and CCl_4, and dried *in vacuo*. Finally, the recovered black powder (0.05 g) and KCN (0.07 g) were boiled in water (10 ml) for 10 min and filtered. The filtrate was evaporated to a volume of 5 ml. After a few days, brown crystals of (I) were filtered and dried on filter paper. An electron-microprobe analysis indicated an Os:S ratio of 1:1.

Crystal data

$K_6[Os_2(CN)_8(SO_2)_2]\cdot 2H_2O$	$Z = 1$
$M_r = 987.31$	$D_x = 2.898$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.9496 (10)$ Å	Cell parameters from 24
$b = 8.9222 (11)$ Å	reflections
$c = 8.9747 (15)$ Å	$\theta = 11.5–14.9°$
$\alpha = 84.202 (15)°$	$\mu = 12.55$ mm^{-1}
$\beta = 64.013 (12)°$	$T = 293 (2)$ K
$\gamma = 81.677 (12)°$	Plate, brown
$V = 565.66 (14)$ Å^3	$0.19 \times 0.16 \times 0.04$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.020$
diffractometer	$\theta_{max} = 25.0°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction: integration	$k = -10 \rightarrow 10$
(*CADDAT*; Enraf–Nonius, 1989)	$l = -9 \rightarrow 10$
$T_{min} = 0.157$, $T_{max} = 0.591$	3 standard reflections
2150 measured reflections	frequency: 60 min
1991 independent reflections	intensity decay: none
1817 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.021$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.054$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 1.39$ e Å^{-3}
1991 reflections	$\Delta\rho_{min} = -1.62$ e Å^{-3}
146 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0010 (3)

Table 1
Selected bond lengths (Å).

Os1—C1	2.048 (6)	Os1—C3	2.059 (6)
Os1—C4	2.050 (6)	Os1—S1^i	2.3198 (15)
Os1—C2	2.052 (7)	Os1—S1	2.3210 (15)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Water H atoms were positioned geometrically, with O—H = 0.82 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(O)$. The deepest
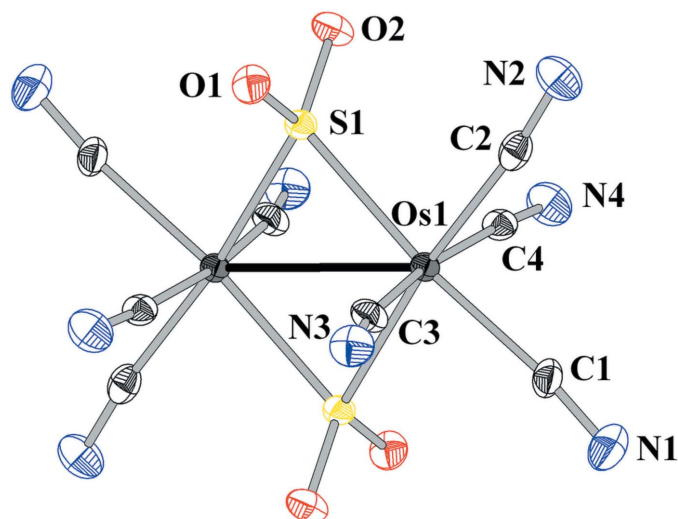

Figure 1
The structure of the $[Os_2S_2O_4(CN)_8]^{6-}$ cluster anion in (I). Displacement ellipsoids are drawn at the 50% probability level and unlabelled atoms are generated by the symmetry operation $(1 - x, -y, 1 - z)$.

hole and highest peak are located at 1.03 Å from atom Os1 and 1.30 Å from atom O1W, respectively.

Data collection: *CD4CA0* (Enraf–Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CADDAT* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *BS* (Kang & Ozawa, 2002); software used to prepare material for publication: *SHELXL97*.

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