$$Na_2[V_2O_4(C_4H_6O_3)_2]\cdot 7H_2O$$

| | | | |
|---|---|---|---|
| V1—O4 | 2.0043(12) | Na1—Na2$^{iii}$ | 3.6806(16) |
| O3—C1 | 1.291(2) | Na2—O4W2 | 2.400(14) |
| O4—C2 | 1.4333(18) | Na2—O3W | 2.416(4) |
| O4—V1$^i$ | 1.9583(12) | Na2—O4W1 | 2.440(3) |
| O5—C1 | 1.234(2) | Na2—O2W$^{ii}$ | 2.4685(19) |
| C1—C2 | 1.523(2) | Na2—O5W | 2.533(5) |
| O5—Na1 | 2.4145(15) | | |
| O1—V1—O2 | 108.03(9) | O3—V1—O4 | 76.49(5) |
| O1—V1—O3 | 98.04(8) | C1—O3—V1 | 119.93(11) |
| O2—V1—O3 | 95.87(7) | C2—O4—V1 | 118.48(9) |
| O1—V1—O4 | 120.15(7) | V1$^i$—O4—V1 | 108.21(5) |
| O2—V1—O4 | 131.77(7) | O3—C1—C2 | 115.80(14) |
| O4$^i$—V1—O4 | 71.79(5) | O4—C2—C1 | 104.53(12) |

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

No attempt was made to model the water H atoms. The Na$^+$ ions were located on a mirror plane at $(x, \frac{1}{4}, z)$. Three and a half water molecules were also located at or near the same mirror plane. One water molecule (O4W) was disordered over two sites and was modelled with site occupancies of 0.83 and 0.17.

Data collection: *COLLECT* (Nonius, 1998). Cell refinement: *DENZO* (Otwinowski & Minor, 1996). Data reduction: *DENZO*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELX97* (Sheldrick, 1998). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELX97*.

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# [*trans*-Bis(en)dioxoosmium(VI)] *trans*-bis(en)dioxoosmium(VI)[aqua-$\eta^1$-sulfato-$\eta^2$-sulfatoiron(II)][diaquabis-($\eta^1$-sulfato)iron(II)] hexahydrate†

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## Abstract

Aqueous ferrous ion reacts reversibly with *trans*-$[Os(en)_2O_2]^{2+}$ producing an intensely blue complex ion which, in the presence of sulfate ion, produces the title complex, $[OsO_2(C_2H_8N_2)_2]_2[Os_2Fe_4O_4(SO_4)_8-(C_2H_8N_2)_4(H_2O)_6]\cdot 12H_2O$, from $H_2O/CH_3OH$ solution. The X-ray structure shows the unit cell to contain two discrete $[Os(en)_2O_2]^{2+}$ ions and two counter-ions having the basic linear core $[(SO_4)_2-Fe-O-Os(en)_2-O-Fe-(SO_4)_2]^{2-}$. Using sulfate ions as bridges, the latter ions form an infinite one-dimensional planar ribbon-like array separated by cations. In this array, the osmyl bond is lengthened [average 1.845(7) Å] with respect to that of the parent ion [average 1.734(7) Å], while the Fe—O bond is shortened to an average of 1.800(6) Å with respect to the usual single-bond distance of 2.05 Å. Sulfate ions serve as bridges between linear cores and are also chelated to a single ferrous ion. The strength of the bonds in the linear Fe—O—Os—O—Fe core as judged by bond-length changes suggests extensive electron delocalization between the metal centers.

## Comment

Some years ago, two related reactions of *trans*-$[Os(en)_2O_2]^{2+}$ were observed (Murmann, 1977). Intensely colored species were reversibly formed with $Fe^{2+}$ and with the photolyzed product of $[Mo(CN)_8]^{4-}$, *i.e.* $[Mo(CN)_7(OH_2)]^{3-}$. The former reaction was studied spectrophotometrically and found to involve two steps forming 1:1 and 1:2 Os–Fe complex ions. It was presumed that these interactions involved coordination of the oxo-O atoms of the highly oxidized osmium complex with a metal ion in a reduced state, but no structural or compositional data are available. These compounds

† Systematic chemical name: poly[bis[*trans*-bis(ethylenediamine)dioxoosmium(VI)] [[hexaaqua-3$\kappa^2O$,4$\kappa O$,5$\kappa^2O$,6$\kappa O$-tetrakis(ethylenediamine)-1$\kappa^4N$,$N'$;2$\kappa^4N$,$N'$-tetra-$\mu$-oxo-1:3$\kappa^2O$;1:6$\kappa^2O$;2:4$\kappa^2O$;-2:5$\kappa^2O$-di-$\mu$-sulfato-3:4$\kappa^2O$:$O'$;5:6$\kappa^2O$:$O'$-tetrasulfato-3$\kappa^2O$;4$\kappa^2$-$O$,$O'$;5$\kappa O$;6$\kappa^2O$,$O'$-tetrairon(II)diosmium(VI)]-di-$\mu$-sulfato-2$\kappa O$:-3'$\kappa O'$;3$\kappa O$:2'$\kappa O'$] dodecahydrate].

are of especial interest because of the possibility of their containing infinite linear polymers having unique electro- or photoelectroconductivity properties and because of the unusual nature of binding of a metal ion to an oxo-O atom. Recent success in preparing single crystals of one component large enough to give a precise X-ray structure has allowed us to answer these structural questions.

The unit cell of the title compound, (I), contains two independent $[Os(en)_2O_2]^{2+}$ cations lying between infinitely polymeric linear ribbons consisting of



(I)
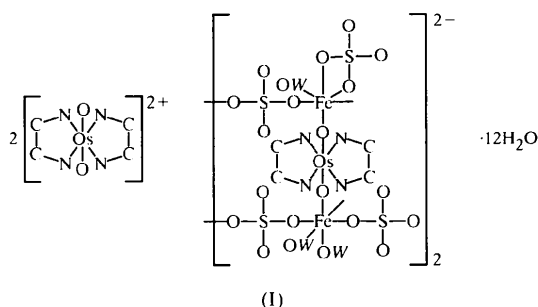
$[Fe_4\{Os(en)_2O_2\}_2]^{12+}$ clusters held together by bridging sulfate ions. Included are 18 water molecules, six of which are coordinated to the iron(II) ions. An OR-TEPIII (Burnett & Johnson, 1996) drawing of one of the two independent cations is shown in Fig. 1. The bond distances and angles in the cations are essentially the same as those reported (Malin et al., 1977) for $[Os(en)_2O_2](HSO_4)_2$. The oxo-O atoms are trans, with an average bond distance of 1.734 (7) Å compared with the previously reported value of 1.74 (1) Å. The ethylenediamine ligands are in the gauche configuration.
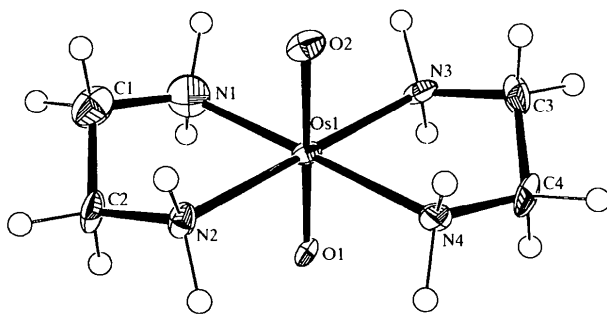


Fig. 1. The molecular structure of one of the cations showing the atom-numbering scheme and the 50% probability displacement ellipsoids.

The linear polymeric anion is essentially planar. The two independent Fe—O—Os—O—Fe clusters are essentially identical and nearly, but not perfectly, repeated through a pseudo-center of symmetry at approximately $0,0,\frac{1}{4}$, which results in a pronounced subcell with $C' = C/2$; Fig. 2 shows all the independent atoms in this

ion. The trans-osmyl atoms bind to iron(II) ions in a nearly linear fashion [average Fe—O—Os and O—Os—O angles are 174 (3) and 178.2 (12)°, respectively], with one osmyl-O atom per iron and two irons per osmium. Four sulfate ions bridge the four dissimilar Fe atoms through oxygen coordination, with the remaining sulfate-O atoms facing into the rectangle formed by the metal ions. Each Fe atom is also coordinated to another sulfate ion through its oxygen(s). Atoms Fe1 and Fe4 are chelated, while Fe2 and Fe3 attach through a single O atom. The $[Fe_4\{Os(en)_2O_2\}_2]^{12+}$ clusters are attached on each side through sulfate-ion bridging attaching Fe1 and Fe3 through the O37 and O39 atoms of the S8 sulfate group, while Fe2 and Fe4 are attached through the O33 and O34 atoms of the S7 sulfate group. This leads to an infinite polymer, as indicated in Fig. 2, where the attaching atoms are shown by arrows. The osmium complexes in these groups have nearly identical bond distances and angles (except for the oxo-O atoms), as in the free cation. No change in the Os—N distance can be discerned. Each $Fe^{II}$ ion is octahedrally coordinated to six O atoms. The positions not associated with sulfate- or oxo-O atoms are filled with water molecules, as shown in Fig. 2. In one sulfate ion, the O atoms show somewhat abnormal displacement parameters. This disorder problem is not severe enough to warrant treatment by partial occupancy of two positions.
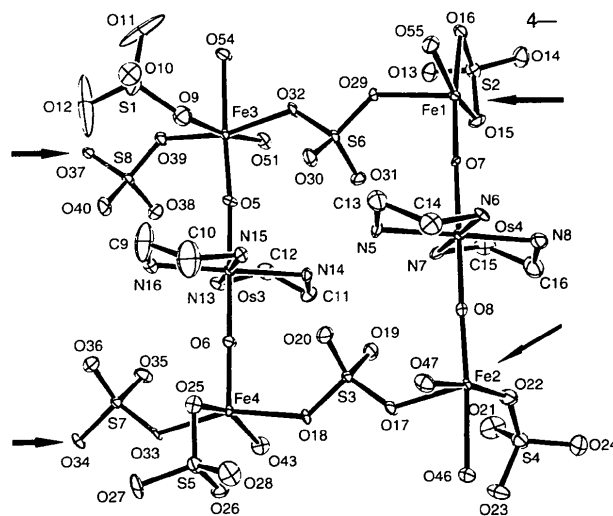


Fig. 2. The molecular structure of the anion showing the atom-numbering scheme and the infinite one-dimensional planar connectivity. Displacement ellipsoids are plotted at the 50% probability level.

The primary interest in this compound is in the bonds between the two metal ions through an O atom. The Os—O bond distance in $[Os(en)_2O_2]^{2+}$ is 1.74 (1) Å (Malin et al., 1977), agreeing with that obtained in this study. In the nearly linear Fe—O—Os—O—Fe

cluster, the average Os—O distance is 1.845 (7) Å. This remarkable lengthening suggests that the Os—O bond has become intermediate between a single and double bond. Conversely, the bond distance to iron(II) is shortened to an average of 1.800 (6) Å from the value usually found (for example, with water or a sulfate ion) of 2.05 Å. Such changes could come about through a reversible one-electron oxidation–reduction process. However, this would result in an increased paramagnetic moment which is not the case (Malin et al., 1977). Furthermore, this would not be expected to result in the intense broad-spectrum light absorption exhibited by the complex ion. Thus, we suggest an explanation involving partial electron transfer from the Fe[II] atom into the bridging O and Os[VI] atoms, with the electron being relatively mobile. Basically, we view this as a very intense labile $d$-electron charge-transfer process which does not lead to irreversible oxidation–reduction. Attraction between these two ions is enhanced by reducing the positive charge on the Fe[II] ion through sulfate-ion coordination. Almost any negative ion capable of coordinating to Fe[II] (such as oxalate, malonate, citrate, phosphate or fluoride) increases its tendency to associate with the osmyl-O atom. It is also facilitated by changing the dielectric constant of the solvent by the addition of methanol. The bridging oxygen no doubt comes from the osmium complex since its exchange rate is extremely slow compared with waters on the Fe[II] atom. The Fe[II] atom binding constants to the oxo-O atom are abnormally large especially considering that $[Os(en)_2O_2]^{2+}$ shows no tendency to protonate even in strong acid solution. It appears that bonding involves $d$-electron transfer from the electron-rich Fe[II] atom to the electron-deficient Os[VI] atom through the oxo-O atom.

The stoichiometry of the compound gives a 1:1 Fe–Os ratio, but the anion responsible for the color has a 2:1 Fe–Os ratio, the counter-ion $[Os(en)_2O_2]^{2+}$ giving the apparent ratio. However, there is clear evidence that a 1:1 complex exists both in solution and the solid state (Murmann, 1977). Crystals isolated previously by the same procedure used here had an entirely different unit cell and 1:1 stoichiometry. Due to their small size, it was not then possible to do a complete structure determination. Those crystals appeared to contain the infinite one-dimensional polymer ion –(O—Os—O—Fe)$_n$–. We intend to carry out an elaborate molecular-orbital bonding calculation on the title compound and this second compound once we are able to determine its crystal structure satisfactorily. Work is continuing on other materials which can be obtained from this system.

## Experimental

The dark-blue complex ion was prepared by the reaction of approximately millimolar aqueous solutions of ferrous

sulfate and pale-yellow $trans$-[Os(en)$_2$O$_2$]Cl$_2$. The latter was prepared as described by Malin & Taube (1971) and Coelho & Malin (1975). A large excess of K$_2$SO$_4$ was added which complexed with the Fe[II] ions, lowering their charge and facilitating reaction with the osmyl-O atoms. Methanol vapor was allowed to diffuse at room temperature into small plastic vessels containing different volumes and concentrations of these solutions. Overnight, a few of these solutions deposited long thin black needles which were collected, washed with methanol and dried. Most crystals were multiple or twinned but a few were shown to be single and satisfactory for X-ray analysis. The other (main) microcrystalline product was shown to have the same chemical analysis and density as the single crystals.

### Crystal data

$[OsO_2(C_2H_8N_2)_2]_2[Os_2$-
$Fe_4O_4(SO_4)_8(C_2H_8N_2)_4$-
$(H_2O)_6]\cdot12H_2O$
$M_r = 2685.71$
Triclinic
$P\overline{1}$
$a = 12.8648\,(7)$ Å
$b = 17.1212\,(10)$ Å
$c = 18.7567\,(11)$ Å
$\alpha = 101.627\,(1)°$
$\beta = 91.701\,(1)°$
$\gamma = 111.515\,(1)°$
$V = 3740.2\,(4)$ Å$^3$
$Z = 2$
$D_x = 2.39$ Mg m$^{-3}$
$D_m = 2.40$ Mg m$^{-3}$
$D_m$ measured by flotation in CCl$_4$/CBr$_4$

Mo $K\alpha$ radiation
$\lambda = 0.70930$ Å
Cell parameters from 6012 reflections
$\theta = 0-27°$
$\mu = 7.86$ mm$^{-1}$
$T = 193$ K
Needle
$0.43 \times 0.05 \times 0.05$ mm
Black

### Data collection

Siemens SMART CCD diffractometer
$\omega$ scans
Absorption correction: empirical ($SADABS$; Blessing, 1995)
$T_{min} = 0.513$, $T_{max} = 0.675$
25 087 measured reflections
15 624 independent reflections

10 951 reflections with $I_{net} > 2.5\sigma(I_{net})$
$R_{int} = 0.030$
$\theta_{max} = 27°$
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 21$
$l = -23 \rightarrow 23$

### Refinement

Refinement on $F$
$R = 0.048$
$wR = 0.059$
$S = 1.19$
10 946 reflections
955 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + 0.0006F^2]$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 4.52$ e Å$^{-3}$ (1.3 Å from Os2)
$\Delta\rho_{min} = -2.42$ e Å$^{-3}$
Extinction correction: none
Scattering factors from Inter-national Tables for X-ray Crystallography (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Os1—O1 | 1.728 (7) | Fe1—O37' | 2.057 (6) |
| Os1—O2 | 1.734 (7) | Fe1—O55 | 2.084 (7) |
| Os1—N1 | 2.112 (8) | Fe2—O8 | 1.808 (6) |
| Os1—N2 | 2.138 (9) | Fe2—O17 | 2.076 (6) |

| | | | |
|---|---|---|---|
| Os1—N3 | 2.115 (9) | Fe2—O22 | 2.040 (8) |
| Os1—N4 | 2.124 (8) | Fe2—O34' | 2.070 (7) |
| Os2—O3 | 1.732 (7) | Fe2—O46 | 2.159 (7) |
| Os2—O4 | 1.740 (7) | Fe2—O47 | 2.089 (7) |
| Os3—O5 | 1.842 (6) | Fe3—O5 | 1.820 (6) |
| Os3—O6 | 1.853 (6) | Fe3—O9 | 2.001 (8) |
| Os3—N13 | 2.130 (8) | Fe3—O32 | 2.090 (6) |
| Os3—N14 | 2.111 (8) | Fe3—O39 | 2.067 (7) |
| Os3—N15 | 2.105 (8) | Fe3—O51 | 2.066 (8) |
| Os3—N16 | 2.093 (9) | Fe3—O54 | 2.135 (7) |
| Os4—O7 | 1.850 (6) | Fe4—O6 | 1.797 (6) |
| Os4—O8 | 1.838 (6) | Fe4—O18 | 2.069 (6) |
| Fe1—O7 | 1.790 (6) | Fe4—O25 | 2.071 (8) |
| Fe1—O15 | 2.075 (8) | Fe4—O33 | 2.071 (6) |
| Fe1—O29 | 2.074 (7) | Fe4—O43 | 2.094 (8) |

| | | | |
|---|---|---|---|
| O1—Os1—O2 | 179.0 (3) | O6—Os3—N15 | 89.1 (3) |
| O1—Os1—N1 | 90.4 (3) | O6—Os3—N16 | 91.2 (3) |
| O1—Os1—N2 | 88.6 (3) | N13—Os3—N14 | 80.4 (3) |
| O1—Os1—N3 | 91.9 (3) | N13—Os3—N15 | 178.7 (3) |
| O1—Os1—N4 | 89.4 (3) | N13—Os3—N16 | 99.3 (3) |
| O2—Os1—N1 | 89.9 (4) | N14—Os3—N15 | 99.3 (3) |
| O2—Os1—N2 | 90.5 (3) | N14—Os3—N16 | 178.9 (3) |
| O2—Os1—N3 | 89.0 (3) | N15—Os3—N16 | 81.0 (3) |
| O2—Os1—N4 | 90.3 (3) | O7—Fe1—O15 | 96.1 (3) |
| N1—Os1—N2 | 80.9 (3) | O7—Fe1—O29 | 98.9 (3) |
| N1—Os1—N3 | 99.4 (3) | O7—Fe1—O37' | 98.7 (3) |
| N1—Os1—N4 | 179.4 (3) | O7—Fe1—O55 | 101.3 (3) |
| N2—Os1—N3 | 179.4 (3) | O15—Fe1—O29 | 92.0 (3) |
| N2—Os1—N4 | 98.5 (3) | O15—Fe1—O37' | 94.6 (3) |
| N3—Os1—N4 | 81.1 (3) | O15—Fe1—O55 | 162.6 (3) |
| O3—Os2—O4 | 177.4 (4) | O29—Fe1—O37' | 160.4 (3) |
| O5—Os3—O6 | 179.0 (3) | O29—Fe1—O55 | 85.6 (3) |
| O5—Os3—N13 | 87.0 (3) | O37'—Fe1—O55 | 82.6 (3) |
| O5—Os3—N14 | 89.4 (3) | Os3—O5—Fe3 | 175.5 (4) |
| O5—Os3—N15 | 91.7 (3) | Os3—O6—Fe4 | 172.3 (5) |
| O5—Os3—N16 | 89.6 (3) | Os4—O7—Fe1 | 171.2 (4) |
| O6—Os3—N13 | 92.2 (3) | Os4—O8—Fe2 | 178.1 (4) |
| O6—Os3—N14 | 89.9 (3) | | |

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$.

H atoms bound to N or C were located easily in difference maps, but water H atoms were not. The former were calculated at ideal positions with isotropic displacement parameters 1.3 times those of the attached atom, while the latter were not included in the least-squares calculations.

Data collection: *SMART* (Siemens, 1997). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1997). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *LSTSQ* in *NRCVAX* (Gabe *et al.*, 1989). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *NRCVAX*.

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# Tricarbonyliron complexes derived from dimethyl 1,3-butadiene-2,3-dicarboxylate: formation of [Fe(CO)₃]₂–dimethyl 1,3-butadiene-2,3-dicarboxylate

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## Abstract

Treatment of dimethyl 1,3-butadiene-2,3-dicarboxylate with $Fe_2(CO)_9$ provided the corresponding tricarbonyl($\eta^4$-dimethyl 1,3-butadiene-2,3-dicarboxylato-$O$)iron, $[Fe(C_8H_{10}O_4)(CO)_3]$, (II), as the main product and the novel $\mu$-[(1,2-$\eta$,$\kappa O^3$:3,4-$\eta$,$\kappa O^2$)-dimethyl 1,3-butadiene-2,3-dicarboxylato]bis(tricarbonyliron), $[Fe_2(C_8H_{10}O_4)(CO)_6]$, (III). In the crystal structure of (II), the electron-deficient butadiene complexes with one $Fe(CO)_3$ group, whereas in (III), the butadiene adopts an unusual conformation and forms a complex with two $Fe(CO)_3$ groups. In (III), each Fe atom possesses a trigonal bipyramidal geometry, with one olefinic bond and two carbonyl ligands occupying the basal positions, and the keto oxygen of the ester and the other carbonyl ligand occupying apical positions.

## Comment

The chemistry of $Fe(CO)_3(\eta^4$-butadiene) complexes has been the subject of intense study and it is now well recognized that these complexes can serve as valuable