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Barium *μ*-*N*,*N'*-Ethylenediaminetetraacetato-di-*μ*-oxo-dioxoditungstate(V) Hydrate

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(*Received* 11 *May* 1978; *accepted* 1 *August* 1978)

Abstract. $\mathrm{Ba[W_2^VO_4(EDTA)]}$. $3\cdot5\mathrm{H_2O}$, $\mathrm{C_{10}H_{12}BaN_2O_{12}W_2.3\cdot5H_2O}$, orthorhombic, $Ima2$ from the systematic absences $h0l$: $l = 2n + 1, h = 2n + 1$; hkl: $h + k + l = 2n + 1$. $a = 19\cdot241\ (4)$, $b = 14\cdot852\ (2)$, $c = 14\cdot091\ (2)$ Å, $Z = 8$, $F(000) = 3368$, $V = 4026\cdot8$ Å^3, $D_c = 3\cdot04$ g cm^{-3}, λ(Cu $K\alpha$, Ni-filtered) = $1\cdot5418$ Å, μ(linear absorption coefficient) = $349\cdot7$ cm^{-1}, $R = 0\cdot054$. Each asymmetric unit consists of two halves of independent molecules, each lying on the mirror plane. The two molecules differ in orientation; one molecule has both W atoms in the mirror plane with an O atom and its mirror image forming the double bridge, while the second molecule has the bridging O atoms in the mirror plane joining an off-plane W and its mirror image. The W–W distances are $2\cdot557$ and $2\cdot542$ Å respectively.

Introduction. Mo is an essential component of several redox enzymes, including nitrogenase, nitrate reductase, xanthine oxidase, sulphite oxidase and formate reductase. Recent reports (Johnson, Cohen & Rajagopalan, 1974; Ljungdahl, 1976) indicate that W is present and has a redox function in some enzymes. A substantial increase in the activity of formate dehydrogenase has been observed when W was substituted for Mo in various experiments (Ljungdahl, 1976). A large number of oxo-Mo$^{\mathrm{V}}$ complexes have been reported (Spivak & Dori, 1975*a*) but stronger reductants are generally required to reduce $\mathrm{W^{VI}} \rightarrow \mathrm{W^{V}}$ (Soares, 1976) and the structure of an oxo-W$^{\mathrm{V}}$ complex containing a $\mathrm{W_2O_4}$ subunit, which is reported in this paper, appears to be the only well-characterized compound of this type.

The crystals were prepared and supplied by A. B. Soares and A. G. Sykes, Department of Inorganic and Structural Chemistry, University of Leeds, as part of aquation and redox studies on a dimeric W$^{\mathrm{V}}$ complex and the Mo analogue.

Analysis of the crystals showed: calculated for $\mathrm{Ba[W_2O_4(EDTA)].2H_2O}$, W 41·2, C 13·5, N 3·14%, found, W 40·0, C 13·1, N 3·25%. A crystal (0·17 × 0·12 × 0·10 mm) was used to collect 1702 unique reflections on an Enraf–Nonius CAD-4 diffractometer with the ω–2θ scan technique and Cu $K\alpha$ (Ni-filtered) radiation ($\lambda = 1\cdot5418$ Å). Orientation and standard-intensity checks were made at fixed intervals. Corrections were made for the Lorentz and polarization effects but no correction was made for absorption.

The space group, $Ima2$, was confirmed from the interatomic vectors on a three-dimensional Patterson synthesis and positions were derived for three heavy atoms, which were assumed to be two W atoms and one Ba atom. These positions were also obtained by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Structure factors were calculated and a three-dimensional Fourier synthesis was produced from the calculated phase angles and observed amplitudes. This showed an additional heavy peak, with sufficient electron density to be taken as a Ba atom, and hence all of the first three heavy-atom positions were now identified as W. At this stage none of the light-atom positions could be clearly identified. Successive structure factor calculations and Fourier syntheses were used to find the light atoms and the final $R = 0{\cdot}054$.* Fractional atomic coordinates are given in Table 1. All computations were carried out using the *SHELX* 76 suite of programs (G. M. Sheldrick, 1976, private communication).

Atomic scattering factors for Ba and W were taken from *International Tables for X-ray Crystallography* (1968). Those for C and O were supplied internally by *SHELX* 76. Anisotropic temperature factors were refined for the metal atoms and the light atoms were refined isotropically. Attempts to use anisotropic temperature factors for the light atoms usually produced non-positive-definite results, possibly due to the fact that no correction for absorption was made. Atoms C(15) and C(35) were refined with fixed x coordinates.

Discussion. Table 2 gives the bond lengths, and Fig. 1 shows a projection of the two molecules of the complex. The W atoms have distorted octahedral coordinations – see Fig. 2 for the W-atom arrangements. The general arrangement of the present structure resembles that of the molybdenum analogue $Mo_2O_3\{K_2C_6H_{13}N_2(COO)_4\}8{\cdot}2H_2O$ (Sheldrick, 1976) and strong similarity exists between the anion unit of the present structure, with the mirror plane passing through the bridging O atoms, and the anion $Mo_2S_2O_2(EDTA)^{2-}$ (Spivak & Dori, 1973). The close similarity between W and Mo is clearly shown by the metal–metal distances and the coordination with the chelating atoms. The present structure has an average W^{v}—W^{v} distance of 2·55 Å compared with the Mo^{v}—Mo^{v} distances of 2·559 Å (Knox & Prout, 1969), 2·541 Å (Cotton & Morehouse, 1965) and 2·552 Å (Delbaere & Prout, 1971) – an average of 2·551 Å.

The angles subtended by the bridging terminal and carboxyl oxygens are shown in Fig. 2. The average W—O distances for the double bridge and terminal oxygens are 1·733 and 1·938 Å respectively. Each W

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses* (×10^3)

Primed atoms are related to unprimed atoms by a mirror plane.

W(1)—W(2)	2·542 (2)	Ba(1)—O(33)	2·776 (31)
W(1)—O(111)	1·746 (52)	C(11)—O(11)	1·238 (47)
W(1)—O(121)	1·957 (30)	C(11)—O(12)	1·194 (47)
W(1)—N(12)	2·471 (21)	C(11)—C(12)	1·508 (53)
W(1)—O(14)	2·032 (31)	C(12)—N(11)	1·493 (54)
W(2)—O(222)	1·696 (46)	C(13)—N(11)	1·497 (25)
W(2)—O(121)	1·883 (30)	C(14)—C(13)	1·501 (26)
W(2)—N(11)	2·469 (40)	C(14)—N(12)	1·485 (25)
W(2)—O(12)	2·057 (31)	C(15)—N(12)	1·522 (20)
W(3)—W(3′)	2·557 (3)	C(16)—C(15)	1·511 (32)
W(3)—O(333)	1·745 (30)	C(16)—O(13)	1·170 (38)
W(3)—O(331)	1·959 (23)	C(16)—O(14)	1·322 (40)
W(3)—O(332)	1·881 (29)	C(31)—O(31)	1·210 (42)
W(3)—N(31)	2·480 (28)	C(31)—O(32)	1·311 (35)
W(3)—O(32)	2·108 (27)	C(31)—C(32)	1·502 (45)
W(3)—O(34)	2·107 (29)	C(32)—N(31)	1·507 (43)
Ba(1)—O(441)	2·835 (28)	C(33)—N(31)	1·501 (45)
Ba(1)—O(442)	2·940 (43)	C(34)—C(33)	1·508 (48)
Ba(1)—O(443)	2·835 (44)	C(34)—O(33)	1·194 (40)
Ba(1)—O(333)	2·842 (26)	C(34)—O(34)	1·268 (39)
Ba(1)—O(11)	2·657 (30)	C(35)—N(31)	1·518 (38)
Ba(1)—O(13)	2·675 (26)	C(35)—C(35′)	1·507 (–)
Ba(1)—O(31)	2·854 (28)	Average W—W = 2·550	
Ba(1)—O(32)	2·958 (24)	Average W—O_t (terminal) = 1·733	
		Average W—O_b (bridging) = 1·938	

Table 1. *Fractional atomic coordinates* (×10^4) *for the complex* Ba[$W^{V}_{2}O_4$(EDTA)].3·5H_2O *with e.s.d.'s in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
W(1)	2500 (0)	5800 (0)	1122 (0)	N(11)	2500 (0)	6084 (13)	−1579 (33)
W(2)	2500 (0)	7027 (1)	−135 (2)	C(13)	2500 (0)	5078 (11)	−1521 (15)
W(3)	1836 (1)	3879 (1)	5942 (2)	C(14)	2500 (0)	4268 (13)	−884 (12)
Ba(1)	−216 (1)	7407 (1)	−3057 (2)	N(12)	2500 (0)	4408 (15)	160 (13)
O(111)	2500 (0)	6429 (34)	2169 (37)	C(15)	1878 (0)	3855 (16)	487 (16)
O(121)	1787 (16)	6236 (20)	245 (21)	C(16)	1502 (12)	4266 (18)	1323 (18)
O(222)	2500 (0)	7939 (31)	589 (32)	O(13)	1051 (14)	3811 (20)	1604 (22)
O(331)	2500 (0)	3243 (20)	5129 (22)	O(14)	1757 (17)	5006 (20)	1713 (21)
O(332)	2500 (0)	4756 (26)	6262 (29)	O(31)	534 (15)	2821 (19)	3873 (21)
O(333)	1607 (14)	3235 (18)	6929 (22)	C(31)	885 (19)	3305 (21)	4369 (18)
O(441)	−321 (15)	1833 (19)	5249 (21)	O(32)	1029 (15)	3163 (18)	5266 (16)
O(442)	−415 (23)	851 (29)	7435 (31)	C(32)	983 (16)	4233 (21)	3966 (30)
O(443)	490 (23)	848 (30)	3042 (32)	N(31)	1536 (13)	4747 (18)	4495 (20)
O(444)	0 (0)	0 (0)	4762 (63)	C(33)	1232 (25)	5615 (22)	4851 (25)
O(11)	1010 (15)	7457 (25)	−2191 (24)	C(34)	878 (15)	5482 (18)	5796 (20)
O(12)	1756 (16)	7516 (23)	−1048 (21)	O(33)	428 (14)	6010 (19)	5972 (28)
C(11)	1521 (18)	7177 (24)	−1746 (25)	O(34)	1083 (16)	4844 (18)	6323 (20)
C(12)	1861 (25)	6333 (23)	−2118 (36)	C(35)	2108 (0)	4934 (33)	3781 (27)

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* Lists of structure factors, thermal parameters, bond angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33827 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

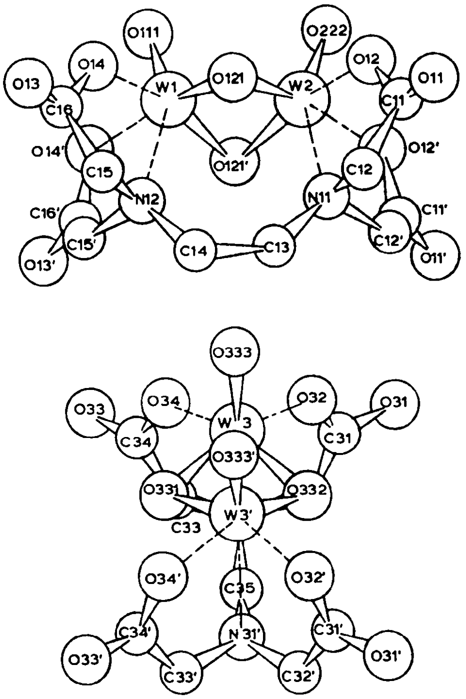

Fig. 1. Projection of two molecules of the complex. The mirror plane passes through W(1), W(2), O(331) and O(332).

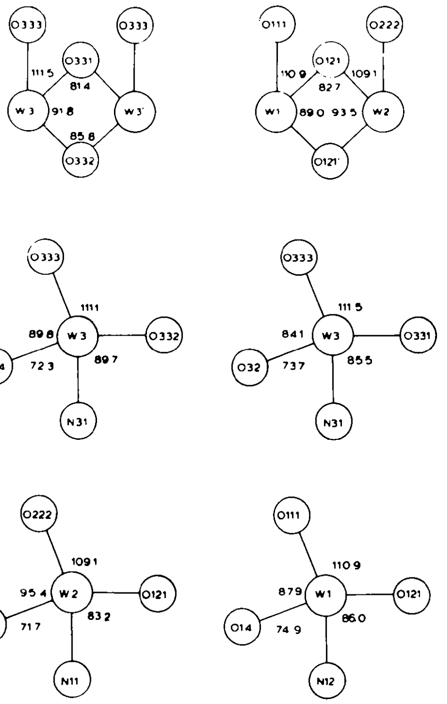

Fig. 2. Schematic diagrams showing the coordination of the W atoms.

is displaced from the best (least-squares) plane defined by the bridging O atoms and the carboxyl O atoms by an average of 0·34 Å, on the same side as the terminal O atoms, giving an average WO$_2$W dihedral angle of 146·7°. Average values for five Mo$_2$O$_4$ type complexes quoted by Spivak & Dori (1975*b*) are Mo—O$_b$ 1·92 Å, Mo—Mo 2·55 Å and Mo—O$_t$ 1·69 Å with dihedral angles in the range 140–150°.

We wish to thank the University of Leeds Computing Service for facilitites.

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