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Tetrapotassium Di-μ-oxo-bis{μ-hydroxo-μ-oxo-μ-*N*,*N'*-ethylenediaminetetraacetate-bis[molybdate(III,IV)]}.16·4H_2O

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Abstract. $Mo_2O_3[K_2C_6H_{13}N_2(COO)_4].8{\cdot}2H_2O$, triclinic $P\bar{1}$; $Z=2$, F.W. 725·4; $a=9{\cdot}893$ (2), $b=11{\cdot}603$ (2), $c=12{\cdot}129$ (3) Å, $\alpha=115{\cdot}65$ (2), $\beta=99{\cdot}16$ (3), $\gamma=77{\cdot}50$ (6)°, $V=1221{\cdot}73$ Å^3; $D_c=2{\cdot}02$ g cm^{-3}; λ(Cu $K\alpha_1$) = 1·54051 Å; $R=0{\cdot}046$. The two Mo atoms and the symmetry-related pair form a planar tetramer with two double and two single O bridges. The angle at the single bridging O is 163·6° with Mo–O = 1·90 Å and each Mo has octahedral coordination.

Introduction. The crystals were prepared and supplied by T. Shibahara and A. G. Sykes of the Department of Inorganic and Structural Chemistry of Leeds University as part of an investigation into the coordination chemistry of Mo. A suitable crystal (0·4 × 0·4 × 0·4 mm) was mounted under nitrogen in a sealed capillary tube containing some mother liquor. Photographs indicate that the space group is triclinic with $Z=2$. Intensities were measured on an Enraf–Nonius CAD-4 diffractometer with the ω–2θ scan technique and graphite-monochromatized Cu $K\alpha$ radiation ($\lambda=1{\cdot}54051$ Å) to $\theta=70°$. 4560 measured reflexions were obtained.

Corrections were applied for absorption by a spherical crystal with $\mu R=2{\cdot}62$ (*International Tables for X-ray Crystallography*, 1962), and for Lorentz and polarization effects.

The structure was solved by the heavy-atom method and refined by full-matrix least squares with isotropic

Table 1. *Fractional atomic coordinates* (× 10^5) *and anisotropic temperature factors* (× 10^4)

Estimated standard deviations are in parentheses. $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{23}klb^*c^*)]$.

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	34565 (5)	68082 (4)	52804 (5)	114 (2)	106 (2)	303 (3)	26 (2)	65 (2)	48 (2)
Mo(2)	43705 (5)	61342 (4)	69118 (5)	135 (2)	99 (2)	283 (3)	15 (2)	55 (2)	31 (2)
K(1)	34113 (15)	26474 (15)	59014 (17)	182 (7)	226 (7)	544 (10)	−8 (6)	57 (7)	57 (7)
K(2)	30453 (21)	60589 (19)	19546 (17)	505 (11)	425 (10)	414 (10)	154 (8)	151 (8)	179 (8)
C(1)	18954 (75)	95326 (69)	56650 (79)	278 (37)	260 (36)	618 (52)	135 (29)	190 (35)	245 (36)
C(2)	31350 (67)	92439 (61)	49335 (66)	217 (32)	182 (31)	385 (39)	−19 (25)	15 (28)	85 (28)
C(3)	4622 (64)	81552 (66)	57969 (68)	119 (29)	289 (35)	413 (40)	38 (25)	72 (27)	105 (31)
C(4)	4463 (66)	72273 (66)	44294 (70)	156 (30)	277 (35)	469 (43)	5 (26)	45 (28)	164 (32)
C(5)	20155 (65)	93123 (59)	75716 (66)	171 (30)	129 (29)	410 (40)	34 (23)	30 (27)	1 (27)
C(6)	19314 (64)	85787 (63)	83227 (67)	140 (30)	215 (32)	409 (40)	21 (24)	45 (27)	21 (29)
C(7)	43168 (67)	85574 (61)	92670 (64)	210 (32)	179 (30)	342 (37)	−51 (25)	11 (27)	3 (27)
C(8)	57403 (68)	77503 (63)	92834 (65)	235 (33)	216 (32)	341 (37)	−54 (26)	6 (27)	67 (28)
C(9)	28524 (74)	71421 (64)	93102 (67)	331 (38)	209 (33)	367 (39)	17 (28)	145 (31)	77 (29)
C(10)	32856 (76)	56848 (68)	88368 (69)	333 (38)	254 (35)	384 (40)	−52 (29)	92 (31)	81 (31)
O(1)	26259 (46)	55782 (44)	57251 (44)	214 (23)	246 (23)	371 (27)	−68 (18)	10 (19)	119 (21)
O(2)	49402 (44)	73999 (41)	65180 (43)	188 (22)	186 (22)	361 (26)	−30 (17)	29 (19)	78 (19)
O(3)	39009 (46)	81490 (43)	46571 (48)	202 (23)	206 (23)	508 (31)	47 (18)	129 (21)	155 (22)
O(4)	32787 (58)	100816 (49)	46270 (55)	467 (33)	260 (26)	625 (37)	23 (23)	210 (28)	242 (26)
O(5)	16243 (45)	66741 (45)	40178 (45)	172 (22)	271 (24)	374 (27)	38 (18)	50 (19)	101 (21)
O(6)	−6731 (52)	70498 (60)	38354 (54)	185 (25)	599 (38)	481 (34)	−44 (24)	−5 (23)	105 (29)
O(7)	59714 (47)	66410 (44)	83938 (45)	219 (23)	221 (23)	358 (27)	35 (18)	21 (20)	30 (20)
O(8)	66013 (54)	82064 (53)	101443 (53)	271 (27)	393 (31)	485 (34)	−78 (23)	−84 (24)	34 (26)
O(9)	37950 (54)	50921 (43)	78114 (45)	452 (30)	154 (22)	354 (27)	−33 (20)	153 (23)	54 (20)
O(10)	30694 (78)	51418 (54)	94528 (57)	993 (53)	281 (29)	496 (36)	−63 (31)	333 (34)	148 (27)
O(11)	44463 (43)	54154 (40)	40017 (43)	171 (21)	162 (21)	371 (26)	28 (16)	82 (18)	109 (19)
O(12)	46552 (91)	26051 (65)	81262 (71)	1009 (64)	407 (37)	736 (50)	6 (39)	208 (45)	264 (36)
O(13)	43798 (71)	1379 (55)	26623 (60)	723 (44)	309 (30)	611 (40)	−203 (29)	201 (34)	72 (28)
O(14)	22584 (60)	32337 (59)	38864 (63)	344 (31)	474 (35)	738 (44)	−141 (26)	121 (29)	144 (32)
O(15)	16093 (89)	3301 (82)	15462 (76)	827 (57)	821 (56)	743 (53)	−359 (46)	60 (43)	125 (44)
O(16)	11304 (83)	82491 (72)	20792 (83)	719 (51)	561 (44)	1101 (67)	47 (38)	214 (46)	384 (46)
O(17)	7135 (91)	24081 (121)	4394 (112)	468 (50)	1581 (105)	1496 (101)	−360 (59)	139 (56)	−337 (81)
O(18)	3400 (66)	58121 (64)	69463 (70)	425 (36)	521 (39)	871 (52)	−82 (30)	111 (34)	220 (37)
O(19)	418 (136)	55496 (149)	13560 (104)	1334 (104)	2056 (144)	886 (78)	−706 (102)	−75 (71)	230 (85)
O(20)	12088 (637)	29845 (638)	86765 (666)	1067 (445)	1341 (519)	1834 (657)	95 (385)	202 (428)	694 (487)
N(1)	18448 (50)	85907 (48)	61888 (52)	124 (24)	162 (25)	382 (31)	43 (19)	79 (22)	103 (23)
N(2)	32352 (53)	77312 (50)	85447 (53)	154 (25)	177 (26)	374 (32)	−4 (20)	51 (22)	58 (23)

temperature parameters until all shifts were less than 3σ ($R=0{\cdot}175$), and then with anisotropic temperature factors to $R=0{\cdot}060$. A difference map at this stage showed the positions of the H atoms and indicated an additional water molecule [O(20)]. The H atoms were added (with isotropic temperature factors of $U_{iso}=0{\cdot}005$) but not refined and the additional O atom introduced with an occupancy factor of 0·2. The final refinement gave $R=0{\cdot}046$.* Final atomic coordinates and temperature factors are given in Table 1, atomic positions for the H atoms in Table 2, and bond lengths and angles in Table 3.

Table 2. *Hydrogen-atom fractional coordinates* ($\times 10^4$)

	x	*y*	*z*
H(1)	2625	4800	5050
H(2)	1066	9780	5234
H(3)	1607	10380	6285
H(4)	−309	8853	6017
H(5)	407	7659	6246
H(6)	1949	8511	7609
H(7)	2802	9728	7709
H(8)	1524	9189	9064
H(9)	1207	8059	8032
H(10)	4498	9094	8904
H(11)	4124	9102	10104
H(12)	3464	7470	10034
H(13)	1859	7291	9301
H(121)	4792	1656	7913
H(122)	4154	3519	8489
H(131)	3770	90	3218
H(132)	4627	1027	3114
H(141)	1470	3293	3273
H(142)	3073	3107	3427
H(151)	1473	914	1117
H(152)	1471	1052	2373
H(161)	1124	8973	1843
H(162)	572	8560	2807
H(171)	1023	2399	1260
H(172)	1750	2200	500
H(181)	−263	6004	7614
H(182)	550	4900	6940
H(191)	59	5120	442
H(192)	996	5036	1391

All computations were carried out with X-RAY 70 (Stewart, Kundell & Baldwin, 1970).

Discussion. The structure (Fig. 1) shows a similarity to the Mo^{III} complex published by Kneale & Geddes (1975), but while the latter has a twofold axis passing between two Mo atoms and between the two C atoms of the ethylene bridge, this compound has a centre of symmetry in the plane of the four Mo atoms. The single bridge O atoms lie 0·008 Å off this plane, which has the equation: $0{\cdot}8553X+0{\cdot}5182Y-0{\cdot}0013Z=7{\cdot}1409$, with orthogonal coordinates on axes respectively parallel to **a**, perpendicular to **a** in the *ac* plane and perpendicular to the *ac* plane.

The angles subtended at the Mo atoms by the bound

Table 3. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Mo(1)–Mo(2)	2·412 (1)	C(10)–O(9)	1·258 (9)
Mo(1)–O(1)	2·075 (6)	C(10)–O(10)	1·231 (13)
Mo(1)–O(2)	1·930 (4)	N(1)—C(1)	1·494 (13)
Mo(1)–O(11)	1·899 (4)	N(1)—C(3)	1·495 (8)
Mo(2)–O(1)	2·087 (4)	N(1)—C(5)	1·517 (9)
Mo(2)–O(2)	1·935 (6)	N(2)—C(6)	1·509 (8)
Mo(2)–O(11)	1·900 (4)	N(2)—C(7)	1·499 (8)
C(2)—O(3)	1·264 (8)	N(2)—C(9)	1·497 (12)
C(2)—O(4)	1·221 (12)	C(1)—C(2)	1·521 (12)
C(4)—O(5)	1·266 (8)	C(3)—C(4)	1·538 (10)
C(4)—O(6)	1·227 (8)	C(5)—C(6)	1·512 (13)
C(8)—O(7)	1·274 (7)	C(7)—C(8)	1·517 (9)
C(8)—O(8)	1·237 (8)	C(9)—C(10)	1·516 (10)

Average C–H = 0·96 (1) Å

O(1)—Mo(1)–O(2)	106·0 (2)	O(1)—Mo(2)–O(2)	105·4 (2)
O(1)—Mo(1)–O(3)	168·4 (2)	O(1)—Mo(2)–O(7)	168·4 (2)
O(1)—Mo(1)–O(5)	83·5 (2)	O(1)—Mo(2)–O(9)	84·4 (2)
O(1)—Mo(1)–O(11)	93·1 (2)	O(1)—Mo(2)–O(11′)	93·3 (2)
O(1)—Mo(1)–N(1)	95·4 (2)	O(1)—Mo(2)–N(2)	97·8 (2)
O(2)—Mo(1)–O(3)	84·2 (2)	O(2)—Mo(2)–O(7)	84·5 (2)
O(2)—Mo(1)–O(5)	165·2 (2)	O(2)—Mo(2)–O(9)	165·6 (2)
O(2)—Mo(1)–O(11)	101·5 (2)	O(2)—Mo(2)–O(11′)	102·2 (2)
O(2)—Mo(1)–N(1)	95·2 (2)	O(2)—Mo(2)–N(2)	91·6 (2)
O(3)—Mo(1)–O(5)	85·4 (2)	O(7)—Mo(2)–O(9)	84·8 (2)
O(3)—Mo(1)–O(11)	89·9 (2)	O(7)—Mo(2)–O(11′)	90·5 (2)
O(3)—Mo(1)–N(1)	78·0 (2)	O(7)—Mo(2)–N(2)	75·5 (2)
O(5)—Mo(1)–O(11)	89·1 (2)	O(9)—Mo(2)–O(11′)	87·5 (2)
O(5)—Mo(1)–N(1)	72·3 (2)	O(9)—Mo(2)–N(2)	76·4 (2)
O(11)–Mo(1)–N(1)	158·4 (2)	O(11′)–Mo(2)–N(2)	159·3 (2)
N(1)—C(1)—C(2)	116·1 (6)	N(2)—C(7)—C(8)	111·9 (5)
C(1)—C(2)—O(3)	117·9 (8)	C(7)—C(8)—O(7)	117·2 (5)
C(1)—C(2)—O(4)	116·7 (6)	C(7)—C(8)—O(8)	118·6 (5)
O(3)—C(2)—O(4)	125·4 (7)	O(7)—C(8)—O(8)	124·2 (6)
N(1)—C(3)—C(4)	108·5 (6)	N(2)—C(9)—C(10)	114·6 (6)
C(3)—C(4)—O(5)	115·7 (5)	C(9)—C(10)–O(9)	118·0 (8)
C(3)—C(4)—O(6)	119·0 (6)	C(9)—C(10)–O(10)	118·2 (7)
N(1)—C(5)—C(6)	117·0 (5)	N(2)—C(6)—C(5)	117·7 (6)
Mo(1)–N(1)—C(1)	107·2 (4)	Mo(2)–N(2)—C(7)	103·5 (4)
Mo(1)–N(1)—C(3)	106·4 (3)	Mo(2)–N(2)—C(9)	109·4 (4)
Mo(1)–N(1)—C(5)	117·4 (4)	Mo(2)–N(2)—C(6)	119·7 (4)

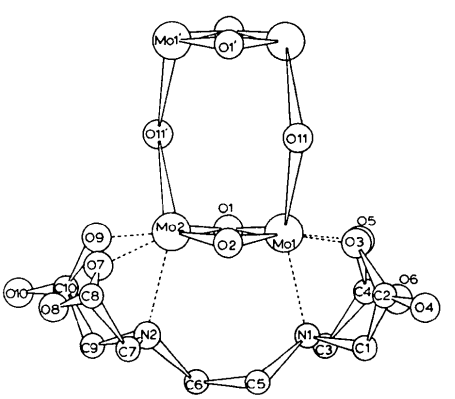

Fig. 1. Perspective view of the asymmetric unit plus atoms connected to the molybdenum atoms. The centre of symmetry is on the plane containing the four molybdenum atoms.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31825 (28 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

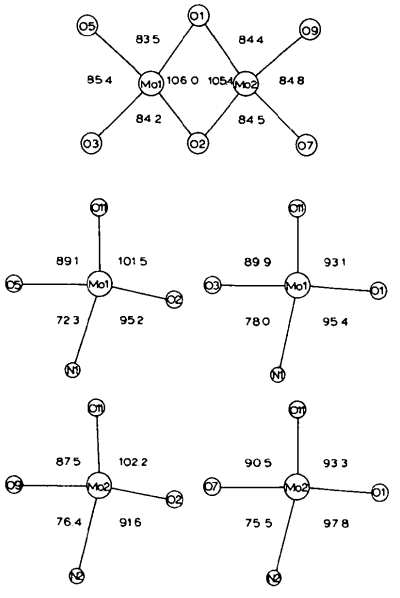

Fig. 2. Schematic views showing the coordination angles around the molybdenum atoms.

atoms are shown in Fig. 2. These vary from 90° by amounts between −18 and +12°; the largest distortions are shown by the angles which include the N atoms, despite the twist of the ethylene bridge. The Mo–Mo bond, 2·412 Å, is a strong metal–metal bond. The single bridge O has Mo–O = 1·899 and 1·900 Å with Mo–O–Mo = 163·6°, which are similar to the values found by Seleborg (1967) for $Na_2Mo_2O_7$ and Le Carpentier, Mitschler & Weiss (1972) for $(pyH^+)_2\{[MoO(O_2)_2H_2O]_2O\}$. The Mo–O distances for the double bridge O atoms are 1·93 and 2·08 Å; the latter, O(1), has a H atom attached.

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6,10-Diaminododecafluorobicyclo[4,4,0]dec-1(10)-en-2-one

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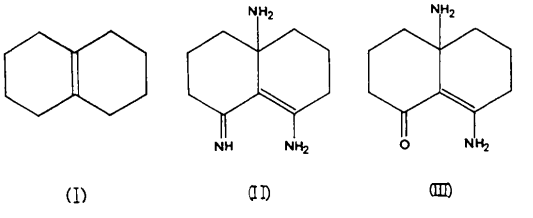
Abstract. $C_{10}H_4F_{12}N_2O$, monoclinic, $P2_1/c$; $a = 11{\cdot}705$ (10), $b = 9{\cdot}73$ (1), $c = 11{\cdot}67$ (1) Å, $\beta = 105{\cdot}91$ (5)°, $U = 1278$ Å^3; $Z = 4$, $D_c = 2{\cdot}058$ g cm^{-3}; μ(Mo $K\alpha$) = 2·4 cm^{-1}. R is 5·69% for 566 observed amplitudes. The measured bond lengths indicate that there is extensive conjugation between the 2-keto and 10-amino groups.

Introduction. Hexadecafluorobicyclo[4,4,0]dec-1(6)-ene (I) reacts readily with dry ammonia in ether to give the diaminoimine (II) which on hydrolysis with dilute acid yields the title compound (III) (Oliver, Stephens, Tatlow & Taylor, 1976). The X-ray analysis was undertaken to confirm the structural assignment and establish the geometry of the molecule.



(I) (II) (III)

(All unmarked substituents are fluorine)

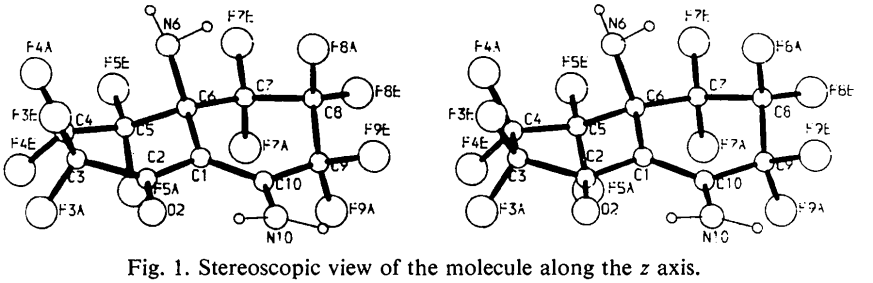


Fig. 1. Stereoscopic view of the molecule along the z axis.