

The Crystal and Molecular Structure of Di- μ -oxo-bis-[2,2'-bipyridyloxohypophosphito-molybdenum(V)]

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$\text{Mo}_2\text{P}_2\text{O}_8\text{N}_4\text{C}_{20}\text{H}_{20}$ crystallizes in the monoclinic space group $P2_1/c$ with $a=9.821$ (4), $b=17.531$ (8), $c=18.111$ (9) Å, $\beta=129.5^\circ$, $Z=4$. With 1907 statistically significant, counter-measured reflexions, the structure was determined by direct and Fourier methods and refined to an R of 0.042. The Mo atoms in the binuclear molecule are doubly bridged by O atoms. There are two terminal O ligands *cis* to the bridging ring, and a monodentate hypophosphito ligand and a bidentate 2,2'-bipyridyl ligand attached to each Mo.

Introduction

At a recent conference devoted to the chemistry and uses of Mo the structure and bonding of molecular oxo-molybdenum species was discussed in terms of their likely importance as catalysts in those life processes where Mo-containing enzymes are known to be involved (Cotton, 1973). The first binuclear complex containing the doubly oxo-bridged $\text{Mo}^{\text{V}}_2\text{O}_4$ group to be structurally characterized was

$\text{Ba}[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (Cotton & Morehouse, 1966). Subsequently, the detailed structures of the Na salt of the cysteinate complex (Knox & Prout, 1969) and of the L-histidinate complex (Delbaere & Prout, 1971), which also contain the $\text{Mo}^{\text{V}}_2\text{O}_4$ group, have been published.

Kergoat & Guerchais (1971) discussed the chemistry, spectra and magnetism of the title compound and suggested that it may contain bridging hypophosphito ligands. A detailed analysis was undertaken at the request of Dr Guerchais and the results are presented here. A preliminary communication has been published (Gatehouse, Guerchais, Kergoat & Nunn, 1976).

Experimental

Samples were provided by Professor J. E. Guerchais, Laboratoire de Chimie Minérale, U.E.R. Sciences, Université de Bretagne Occidentale, France. A crystal, approximately cubic in shape, of about 0.3 mm length was mounted on a Philips PW 1100 automatic four-circle diffractometer. The crystal was monoclinic with systematic absences consistent with the space group $P2_1/c$ (*International Tables for X-ray Crystallography*, 1952).

The cell parameters reported in Table 1 were obtained by least-squares refinement of the reciprocal spacings for particular reflexions. The zones measured were $h00$, $0k0$, $hh0$, $h0h$, $00l$, $0kk$ with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å), and an upper limit of $\theta=30^\circ$. Where possible, the four reflexions in each zone with

the highest value of intensity times $\tan\theta$ were used. The centres of these peaks and of their anti-reflexions were determined and used in the refinement of the reciprocal lattice spacing. Intensities were collected with graphite-monochromated Mo $K\alpha$ radiation and a take-off angle of 6° . A θ - 2θ scan was used with a constant width $\Delta\theta=1.2^\circ$, a speed of $0.05^\circ \text{ s}^{-1}$ and an allowance for dispersion. Two background measurements, each for half the scan time, were made for each scan, one at the lower and one at the upper limit. Three non-coplanar standard reflexions were measured every 2h and showed no significant variation in θ or intensity.

Table 1. Crystallographic data for Di- μ -oxo-bis-[2,2'-bipyridyloxohypophosphito-molybdenum(V)]

Crystal system	Monoclinic
Space group	$P2_1/c$
a	9.821 (4) Å
b	17.531 (8)
c	18.111 (9)
β	129.5 (2)°
V	2405.8 Å ³
Z	4
D_c	1.93 g cm ⁻³
D_m	1.93
$\mu(\text{Mo } K\alpha)$	12.16 cm ⁻¹

The data were corrected for Lorentz and polarization effects. Since the plane of reflexion of the monochromator was perpendicular to that of the specimen crystal, the Lorentz-polarization correction was

$$(\text{Lp})^{-1} = \sin 2\theta(1 - \cos^2 2\theta_m)/(\cos^2 2\theta + \cos^2 2\theta_m),$$

where $\theta_m=13.2^\circ$ was the Bragg angle of the monochromator. The variance of the structure amplitude was then $\sigma^2(F) = \sigma^2(I) (\text{Lp})^{-2}/4F^2$. Of the 2229 unique reflexions measured, 322 were considered to be statistically insignificant [$I \leq 3\sigma(I)$] and were given zero weight during the solution and refinement of the structure.

The scattering factor curve for P⁰ was that of Cromer & Waber (1965), those for Mo⁰, C⁰, N⁰, O⁰, H⁰ were from Ibers (1962). All computing was performed on the Monash University CDC 3200 computer. The direct-methods programs used in the solution of the structure were *WILSE*, a local adaptation of a program by Shiono (1964) which obtained the scale and overall temperature factor from a Wilson plot (Wilson, 1942) and calculated normalized structure factors (Karle & Hauptman, 1956), and the *MULTAN* series of Germain, Main & Woolson (1970) for the calculation of phases. Other programs used were *MONLS*, a local version of the full-matrix least-squares program of Busing, Martin & Levy (1962), *MONDLS*, a block-diagonal least-squares refinement program adapted from the 'SF series' of Shiono (1968) and the Fourier summation program *MONFR* (White, 1965). The thermal ellipsoid program *ORTEP* (Johnson, 1965) was used to produce stereoscopic diagrams of the structure.

Solution and refinement of the structure

The positions of the two Mo atoms were determined by direct methods and confirmed from a Patterson summation.

The 431 reflexions with $E \geq 1.3$ were used as input to *MULTAN*. An E map indicated the positions of the two Mo atoms. After variation of the scale, the calculation of the structure factors was performed on the basis of two Mo atoms and yielded $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.5$. Trial positions for all C, N and O atoms attached to Mo and improved Mo positions were obtained from a difference synthesis. Two cycles of full-matrix least-squares refinement of all the trial positional parameters resulted in an R of 0.29. A further difference synthesis located the P atoms and the O atoms attached to P. Refinement of the trial positions led to an R of 0.18. By first of all including the isotropic temperature factors in the refinement to an R of 0.11, and then using a block-diagonal least-squares refinement with the Mo atoms varying anisotropically, we obtained an R of 0.056. A difference synthesis indicated anisotropy for the Mo=O oxygen atoms and the atoms in each O-P-O grouping, especially

the terminal O. Three further cycles of refinement, with anisotropic thermal parameters for these atoms also, yielded an R of 0.047. The final positional and thermal parameters are listed in Table 2. A difference synthesis at this stage yielded the positions of most of the H atoms. All the H atom positions were idealized with C-H 1.05 Å and trigonal geometry at the C and tetrahedral at the P atoms. These idealized coordinates are given in Table 3. A final structure factor calculation with all H atoms included and each given an isotropic temperature factor 1 Å² greater than the B value of the associated C or P atom gave R 0.042.*

A difference map calculated from the final parameters revealed some maxima and minima with values up to $\pm 0.6 e \text{ \AA}^{-3}$, close to the calculated positions for H atoms.

Description of the structure

The molecular structure is illustrated in Fig. 1 and the packing in Fig. 2. The complex is binuclear with each Mo coordinated to two bridging and one terminal O, a bidentate 2,2'-bipyridyl ligand and an O of a monodentate hypophosphito ligand, resulting in a distorted octahedral environment for each Mo, the octahedra sharing a common edge. The two Mo-O bonds on each bridge have an average length of 1.933 (10) Å. The two terminal O atoms *cis* to the bridging

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31750 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

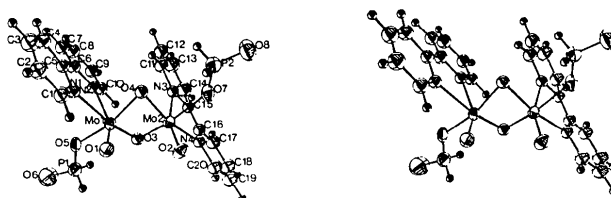


Fig. 1. Stereoscopic diagram of the title compound. The numbering is consistent with Table 2. The hydrogen atoms have not been labelled.

Table 2. Final positional and thermal parameters in di- μ -oxo-bis-[2,2'-bipyridyloxohypophosphitomolybdenum(V)]

Non-hydrogen positions are multiplied by 10⁴. B is the Debye-Waller temperature factor. The anisotropic temperature factor is of the form: $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^{-4}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	3897 (2)	3801 (1)	1019 (1)	306 (7)	344 (9)	298 (9)	14 (5)	219 (5)	33 (6)
Mo(2)	4304 (2)	4002 (1)	2546 (1)	276 (6)	299 (9)	304 (9)	-11 (5)	206 (5)	1 (6)
O(1)	4012 (15)	4715 (6)	7893 (8)	723 (78)	293 (76)	551 (83)	81 (55)	502 (65)	110 (56)
O(2)	4195 (14)	4960 (6)	2529 (8)	573 (70)	278 (74)	569 (81)	6 (51)	428 (60)	-7 (61)
O(5)	1796 (13)	3581 (7)	-412 (8)	401 (63)	824 (96)	288 (71)	151 (57)	244 (50)	35 (59)
O(6)	-1235 (18)	3477 (9)	-2032 (10)	638 (87)	1240 (136)	551 (96)	169 (84)	162 (69)	-158 (86)
O(7)	6359 (13)	3971 (6)	4028 (7)	411 (61)	516 (80)	339 (70)	-77 (50)	274 (49)	-38 (53)
O(8)	9371 (15)	4008 (9)	5656 (9)	455 (72)	1123 (121)	431 (83)	-67 (70)	253 (59)	-119 (75)
P(1)	-162 (6)	3691 (3)	-1038 (3)	386 (25)	579 (36)	358 (30)	38 (20)	206 (19)	-45 (22)
P(2)	8319 (5)	3854 (3)	4619 (3)	352 (23)	456 (33)	383 (30)	-38 (19)	232 (18)	-17 (21)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C(1)	6685 (20)	4074 (10)	701 (12)	3.3 (3)
C(2)	8030 (22)	3904 (10)	663 (13)	3.8 (4)
C(3)	8469 (22)	3170 (10)	697 (13)	4.1 (4)
C(4)	7597 (21)	2586 (10)	751 (12)	3.4 (4)
C(5)	6230 (18)	2782 (9)	763 (11)	2.5 (3)
C(6)	5120 (19)	2201 (9)	760 (11)	2.9 (3)
C(7)	5210 (20)	1429 (10)	613 (12)	3.4 (3)
C(8)	4088 (21)	941 (10)	605 (12)	3.7 (4)
C(9)	2953 (20)	1219 (9)	731 (11)	3.2 (3)
C(10)	2929 (19)	1995 (9)	857 (11)	2.9 (3)
C(11)	5130 (20)	2203 (10)	3032 (12)	3.3 (3)
C(12)	4877 (22)	1453 (10)	3155 (13)	3.9 (3)
C(13)	3548 (24)	1300 (11)	3166 (14)	4.8 (4)
C(14)	2478 (23)	1882 (11)	3086 (14)	4.5 (4)
C(15)	2841 (18)	2624 (9)	2991 (11)	2.6 (3)
C(16)	1953 (19)	3298 (9)	2973 (11)	2.8 (3)
C(17)	648 (22)	3257 (10)	3082 (13)	3.9 (4)
C(18)	-12 (23)	3937 (11)	3118 (13)	3.3 (4)
C(19)	553 (22)	4610 (11)	3067 (13)	4.2 (4)
C(20)	1826 (21)	4623 (10)	2941 (12)	3.6 (4)
N(1)	5801 (15)	3512 (7)	759 (9)	2.6 (2)
N(2)	4013 (15)	2488 (7)	882 (9)	2.6 (2)
N(3)	4113 (14)	2771 (7)	2937 (8)	2.3 (2)
N(4)	2474 (14)	3966 (7)	2885 (8)	2.6 (2)
O(3)	2270 (12)	3680 (6)	1266 (7)	2.4 (2)
O(4)	5913 (12)	3648 (6)	2360 (7)	2.5 (2)

Table 3. Idealized positional coordinates ($\times 10^3$) for the hydrogen atoms

The hydrogen atoms attached to carbon are numbered according to the appropriate carbon atom. The hydrogen atoms attached to phosphorus are designated by the number of the phosphorus, *a* and *b* refer to the two hydrogens on each phosphorus.

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	636	465	69
H(2)	872	435	62
H(3)	949	303	67
H(4)	795	202	78
H(7)	608	123	50
H(8)	410	35	50
H(9)	211	85	73
H(10)	204	221	94
H(11)	614	233	301
H(12)	573	101	325
H(13)	327	72	323
H(14)	145	155	311
H(17)	18	273	312
H(18)	-98	392	320
H(19)	6	512	313
H(20)	226	515	288
H(P1a)	-61	337	-74
H(P1b)	-39	427	-101
H(P2a)	865	344	447
H(P2b)	867	442	440

ring have an average Mo=O distance of 1.680 (12) Å. Within the plane of the bridging ring the average Mo-O distance to the bonding O of the hypophosphito ligand is 2.088 (9) Å. Each Mo is displaced from the mean plane through the bridging O atoms, the O of the coordinated hypophosphito ligand and the appropriate bipyridyl N atoms, the displacement averaging 0.34 Å [Mo(1) 0.334 (0.002), Mo(2) 0.355 (0.002)]. The angle between the two MoO₂ bridge

planes is 143°. Knox & Prout (1969) have reported a similar bridging geometry in Na₂Mo₂O₄(cysteine)₂·5H₂O, for which each Mo was 0.38 Å out of the plane of the bridging O atoms and the N and S coordinated from cysteine, the MoO₂ dihedral angle being 150°. These authors also reported Mo-O_{br} distances of 1.93 Å and an Mo=O distance of 1.71 Å, with the bond *trans* to the π system of the Mo=O bond lengthened. The average Mo-N (*trans*) distance in this compound is 2.32 (1) Å compared to 2.25 (1) Å for the other Mo-N bond.

The bipyridyl ligands are distorted from planarity. The deviations from the mean plane through the two bridging C and the N from the shorter Mo-N bond are listed in Table 4. The Mo atoms are out of these planes by 0.378(1) for Mo(1) and 0.320(1) Å for Mo(2).

Table 4. Deviations of atoms from mean planes (Å $\times 10^3$)

Standard deviations are in parentheses.

(a) The plane through N(1), C(5), C(6) is
 $0.0061X - 0.0025Y - Z = -1.0474$

Mo(1)	-378 (1)	C(4)	27 (17)
N(2)	-178 (13)	C(7)	211 (17)
C(1)	85 (17)	C(8)	217 (17)
C(2)	146 (19)	C(9)	33 (15)
C(3)	105 (18)	C(10)	-148 (15)

(b) The plane through N(4), C(15), C(16) is
 $0.0676X + 0.0695Y + 0.9953Z = 4.4381$

Mo(2)	320 (1)	C(14)	-10 (20)
N(3)	-31 (11)	C(17)	-51 (18)
C(11)	-155 (17)	C(18)	-137 (18)
C(12)	-208 (18)	C(19)	-190 (18)
C(13)	-115 (20)	C(20)	-111 (7)

Table 5. Bond distances (Å) and angles (°) in *di-μ-oxo-bis*-[2,2'-bipyridyloxohypophosphito-molybdenum(V)]

Estimated standard deviations are in parentheses ($\times 10^3$ for distances, $\times 10$ for angles).

(a) Bond distances

Mo(1)—O(1)	1.678 (12)	Mo(2)—O(2)	1.682 (11)
Mo(1)—O(3)	1.924 (15)	Mo(2)—O(3)	1.949 (8)
Mo(1)—O(4)	1.944 (8)	Mo(2)—O(4)	1.916 (14)
Mo(1)—O(5)	2.080 (9)	Mo(2)—O(7)	2.097 (9)
Mo(1)—N(1)	2.258 (18)	Mo(2)—N(3)	2.316 (13)
Mo(1)—N(2)	2.325 (12)	Mo(2)—N(4)	2.240 (18)
N(1)—C(1)	1.360 (26)	N(3)—C(11)	1.341 (24)
C(1)—C(2)	1.398 (35)	C(11)—C(12)	1.383 (26)
C(2)—C(3)	1.346 (27)	C(12)—C(13)	1.346 (38)
C(3)—C(4)	1.377 (31)	C(13)—C(14)	1.403 (33)
C(4)—C(5)	1.400 (32)	C(14)—C(15)	1.388 (27)
C(5)—C(6)	1.489 (27)	C(15)—C(16)	1.457 (25)
C(6)—C(7)	1.393 (24)	C(16)—C(17)	1.417 (35)
C(7)—C(8)	1.388 (31)	C(17)—C(18)	1.377 (30)
C(8)—C(9)	1.362 (35)	C(18)—C(19)	1.332 (30)
C(9)—C(10)	1.382 (23)	C(19)—C(20)	1.407 (38)
C(5)—N(1)	1.346 (21)	C(11)—N(3)	1.341 (24)
C(10)—N(2)	1.350 (25)	C(20)—N(4)	1.351 (25)
O(5)—P(1)	1.500 (12)	O(7)—P(2)	1.494 (12)
O(6)—P(1)	1.422 (15)	O(8)—P(2)	1.462 (14)
Mo(1)—Mo(2)	2.554 (3)		

Table 5 (cont.)

(b) Bond angles

N(1)—Mo(1)—N(2)	69.7 (5)	O(3)—Mo(1)—O(4)	91.8 (5)	N(4)—Mo(2)—O(3)	85.6 (5)
N(1)—Mo(1)—O(1)	88.1 (6)	O(3)—Mo(1)—O(5)	87.5 (5)	N(4)—Mo(2)—O(7)	86.3 (5)
N(1)—Mo(1)—O(4)	84.8 (5)	Mo(1)—O(5)—P(1)	134.3 (8)	O(2)—Mo(2)—O(3)	105.3 (6)
N(1)—Mo(1)—O(5)	89.7 (5)	O(5)—P(1)—O(6)	118.6 (9)	O(2)—Mo(2)—O(4)	111.7 (6)
N(2)—Mo(1)—O(3)	91.2 (5)	Mo(1)—O(3)—Mo(2)	82.5 (4)	O(2)—Mo(2)—O(7)	92.8 (6)
N(2)—Mo(1)—O(5)	76.1 (5)	N(3)—Mo(2)—N(4)	69.8 (5)	O(4)—Mo(2)—O(3)	91.9 (5)
N(2)—Mo(1)—O(4)	85.3 (5)	N(3)—Mo(2)—O(3)	82.7 (5)	O(4)—Mo(2)—O(7)	89.2 (5)
O(1)—Mo(1)—O(3)	111.1 (6)	N(3)—Mo(2)—O(4)	89.3 (5)	Mo(2)—O(7)—P(2)	132.2 (8)
O(1)—Mo(1)—O(4)	105.4 (6)	N(3)—Mo(2)—O(7)	77.5 (5)	O(7)—P(2)—O(8)	117.1 (8)
O(1)—Mo(1)—O(5)	92.2 (6)	N(4)—Mo(2)—O(2)	88.9 (6)	Mo(1)—O(4)—Mo(2)	82.9 (5)

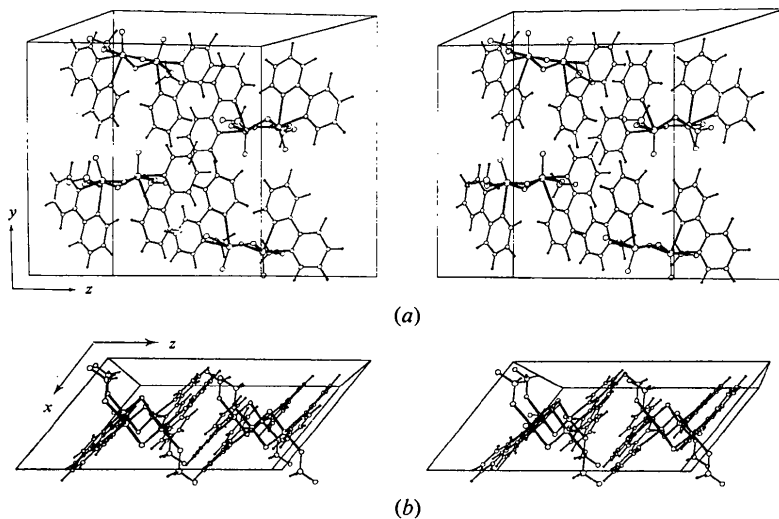


Fig. 2. Stereoscopic diagrams of the molecular packing in the title compound.

The hypophosphito ligands have average P—O distances of 1.452(14) and 1.497(12) Å, the longer being to the O coordinated to Mo. The OPO angle averages 118(1)°. These values may be compared with 1.51 Å and 120 ± 8° found in ammonium hypophosphite (Zachariassen & Mooney, 1934).

The terminal O atoms of the hypophosphito ligand have anisotropic temperature factors which are larger than those of any of the other atoms in the molecule.

The packing diagram shows that the terminal hypophosphito O atoms approach some of the bipyridyl H atoms of neighbouring molecules to about 2.4–2.5 Å, indicating a certain amount of hydrogen bonding between molecules.

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