Preparation and Characterization of bis(2-thiopyrimidinato)bis(pyridine)-dioxodi(μ-oxo)dimolybdenum(V)

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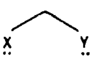
The reaction of $Mo_2(O_2CCH_3)_4$ *with 2-mercaptopyrimidine gave a green solid which was transformed by dissolving in pyridine in air to a red-orange crystalline product which has been shown by X-ray crystallography to be* $[MoO(NC_5H_5)(SN_2C_4H_3)]_2(\mu\text{-}O)_2$. *The molecule has the familiar oxo-bridged dinuclear structure with the Mo–O bonds cisoid and distorted octahedra completed about each metal atom by a pyridine nitrogen atom, a pyrimidine nitrogen atom and the pyrimidine sulfur atom. No crystallographic symmetry is imposed but the molecule closely approximates* C_2 *symmetry. The Mo–Mo distance is 2.576(1)Å. The crystallographic parameters are: Space group,* $P\bar{1}$; *a = 12.063(7)Å; b = 12.149(5)Å; c = 10.362(5)Å;* α *= 98.51(3)°;* β *= 104.84(4)°;* γ *= 102.91(4)°; V = 1396(1)Å*^{3}*; Z = 2. Using 3389 data with* $F_o^2 > 3\sigma(F_o^2)$ *and 313 variables, the structure was refined by full-matrix least squares to final discrepancy indices of* R_1 *= 0.044 and* R_2 *= 0.073.*

Introduction

It is well known [1] that bidentate anionic ligands of type *1*, such as RCO_2^-, 2-oxopyridine, *etc.* serve to stabilize dinuclear quadruply-bonded complexes



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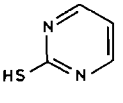
containing M_2^{m+} units, either by reaction with the group VI hexacarbonyls or with $Mo_2(O_2CCH_3)_4$. With the initial objective of obtaining a Mo_2^{4+} complex, we carried out the reaction of $Mo_2(O_2CCH_3)_4$ with 2-mercaptopyrimidine, *2*.



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We did not detect any such product, *e.g.*, $Mo_2(SN_2C_4H_3)_4$, but instead we obtained and structurally characterized a binuclear oxomolybdenum(V) compound.

Experimental

Preparation

Dimolybdenum tetraacetate (0.214 g; 0.50 mmol), and 2-mercaptopyrimidine (0.222 g; 2.00 mmol) were added to a 100 ml round-bottom flask containing 30 ml of dry methanol. This mixture was stirred at *ca.* 30 °C for one hour and then filtered to collect a green, air-stable precipitate. The precipitate was found to be insoluble in most of the common solvents, but it dissolved in pyridine to give a green solution. Upon standing in the air this solution became red-orange within minutes. Subsequent air evaporation of this solution gave red-orange crystals of the title compound.

X-Ray Data Collection

A suitable crystal was coated with epoxy and secured to the end of a thin glass fiber with epoxy cement. The crystal was shown to be of good quality by ω-scans of several intense reflections which had peak widths at half-height of *ca.* 0.2°. Lattice parameters and other crystal data are summarized in Table I.

Data were collected at 22 ± 2 °C using a Syntex $P\bar{1}$ autodiffractometer, with graphite-monochromatized Mo K_α radiation and the θ–2θ scan technique. Variable scan rates from 4 to 24°/min were used, depending upon the intensity of the reflection, with a scan range from (Mo $K_{\alpha 1}$) – 1.0° to (Mo $K\alpha_2$) + 1.0°. The absence of any systematic absences was consistent with the space group $P\bar{1}$. Three standard reflections were measured every 100 reflections and showed no significant decrease in intensity during data collection. The usual Lorentz and polarization corrections were applied but absorption corrections were omitted [2].

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TABLE I. Crystallographic Parameters.

Formula	$Mo_2C_{23}H_{21}N_7S_2O_4$
Form. wt.	715.48
Space Group	$P\bar{1}$
a, Å	12.063(7)
b, Å	12.149(5)
c, Å	10.362(5)
α, deg.	98.51(3)
β, deg.	104.84(4)
γ, deg.	102.91(4)
V, Å^3	1396(1)
d_{calcd}, g/cm^3	1.701
Z	2
Crystal size, mm.	0.25 × 0.35 × 0.50
μ(Mo K_α), cm^{-1}	10.692
Range 2θ, deg.	0.01–45
No. unique data	3666
No. Data, $F_o^2 > 3\sigma(F_o^2)$	3389
No. variables	313
R_1	0.044
R_2	0.073
Goodness of fit	1.931
Largest Δ/σ^a	0.26

$^a\Delta/\sigma$ represents parameter shift divided by esd in final cycle of least squares refinement.

Solution and Refinement

The positions of the two crystallographically independent molybdenum atoms were determined from the solution of the three-dimensional Patterson function [2]. The remaining non-hydrogen atoms were located from successive Fourier and difference syntheses. Full-matrix anisotropic least-squares refinement of all atoms except the lattice pyridine, yielded the figures of merit listed in Table I. The final discrepancy indices are defined by the expressions:

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors were those of Cromer and Waber [3]. Anomalous dispersion effects were also included for the molybdenum atoms [4].

Results

A perspective view of the molecule is presented in Fig. 1, which also defines the atomic numbering scheme used. The atomic positional parameters are given in Table II and the bond distances and angles are given in Tables III and IV.

Each molecule occupies a general position within the unit cell of the triclinic space group $P\bar{1}$. Associated with each dimolybdenum molecule is an additional pyridine molecule that occupies the voids between the dimolybdenum molecules. These lattice pyridine molecules are disordered, as indicated by the rather large thermal parameters associated with each atom. Since it was impossible to identify, with certainty, which of the six atoms was the nitrogen, all atoms were refined as carbon atoms.

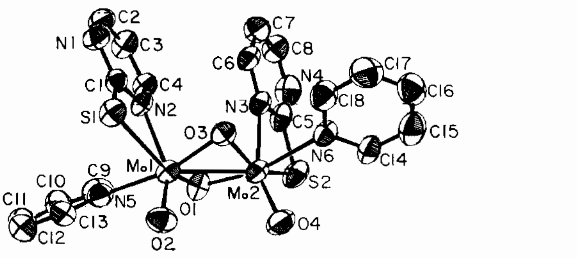

Fig. 1. An ORTEP computer drawn representation of the $Mo_2O_4(SN_2C_4H_3)_2(NC_5H_5)_2$ molecule. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of the electron density.

Each molybdenum atom in *1* is coordinated to three mutually *cis* oxygen atoms (two bridging, one non-bridging), one thiopyrimidinato anion, and a pyridine molecule. The geometry about each molybdenum can be described as a distorted octahedron. Although the entire binuclear molecule is the crystallographic asymmetric unit and no rigorous symmetry is required, it comes very close to having C_2 symmetry, with the C_2 axis being a perpendicular bisector of both the O(1)···O(3) and Mo(1)–Mo(2) internuclear lines. As far as Mo to ligand bond distances are concerned the pairwise equivalences demanded by C_2 symmetry are closely approximated. No such pair differs by more than 0.029 Å and the average of these discrepancies is only 0.012 Å.

The C_2 symmetry would not require all of the Mo–O(br) distances to be equal, but in fact they very nearly are. Those *trans* to the Mo–S bonds have a mean length of 1.942 ± 0.014 Å and those *trans* to the Mo–N bonds average 1.954 ± 0.007 Å. The central $Mo_2(\mu\text{-}O)_2$ ring is markedly buckled with the Mo atoms above and the μ-O atoms below the mean plane by an average of 0.186 Å. This allows the Mo atoms to approach closely enough, 2.576(1)Å, to form a single bond. There is a slight twist in the central $Mo(O)(\mu\text{-}O)_2Mo(O)$ group such that the O=Mo–Mo=O chain has a torsional angle of 7.0°.

As is usual in polyoxo species of Mo(V) and Mo(VI) [5] the O–Mo–O angles are larger than 90° resulting in compression of the other angles subtended at the metal atom by ligand atoms. It is in this sense that the angular distortions from regular octahedral symmetry can be understood.

Discussion

The compound whose structure is reported here, and the method of preparation, should be compared

TABLE II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2O_4(SN_2C_4H_3)_2 \cdot 3NC_5H_5$.

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Mo(1)	0.74375(3)	0.08093(3)	0.20230(4)	3.99(1)	3.42(1)	3.13(1)	1.12(1)	1.07(1)	0.79(1)
Mo(2)	0.88771(3)	0.23470(3)	0.13197(4)	4.47(1)	3.72(1)	3.19(1)	1.68(1)	1.42(1)	1.47(1)
S(1)	0.7660(1)	−0.09305(9)	0.3103(1)	5.03(5)	2.73(4)	4.20(5)	0.76(4)	1.13(4)	0.51(4)
S(2)	0.9555(1)	0.45655(10)	0.1964(1)	6.93(5)	3.84(4)	5.31(5)	2.56(4)	2.52(4)	2.46(4)
O(1)	0.7676(3)	0.2482(3)	0.2256(3)	5.6(1)	3.8(1)	4.1(1)	1.0(1)	2.36(9)	1.2(1)
O(2)	0.6414(3)	0.0050(3)	0.0540(3)	4.5(1)	5.4(1)	3.8(1)	1.4(1)	0.6(1)	0.1(1)
O(3)	0.9011(2)	0.0902(2)	0.1811(3)	4.1(1)	3.4(1)	3.6(1)	1.20(9)	1.11(9)	1.0(1)
O(4)	0.8242(3)	0.2211(3)	−0.0360(3)	5.9(1)	6.5(2)	3.9(1)	2.5(1)	1.5(1)	2.1(1)
N(1)	0.8872(3)	−0.0078(3)	0.5794(4)	4.8(1)	3.7(1)	4.0(2)	1.4(1)	0.8(1)	1.2(1)
N(2)	0.8338(3)	0.1195(3)	0.4356(3)	4.5(1)	2.7(1)	3.4(1)	1.0(1)	1.4(1)	1.3(1)
N(3)	1.0321(3)	0.3181(3)	0.3375(3)	4.3(1)	2.9(1)	3.8(1)	1.1(1)	1.5(1)	1.4(1)
N(4)	1.1198(4)	0.5169(3)	0.4486(5)	6.6(2)	3.0(1)	6.5(2)	0.9(1)	2.6(2)	1.0(1)
N(5)	0.5897(3)	0.0854(3)	0.2904(4)	4.5(1)	4.6(2)	4.1(2)	1.7(1)	1.1(1)	1.4(1)
N(6)	1.0619(3)	0.2398(3)	0.0836(4)	5.0(1)	4.2(1)	3.5(1)	1.9(1)	1.9(1)	1.4(1)
C(1)	0.8354(4)	0.0136(3)	0.4573(4)	3.7(2)	2.7(1)	4.2(2)	0.7(1)	1.4(1)	1.1(1)
C(2)	0.9351(4)	0.0840(4)	0.6838(5)	5.1(2)	4.4(2)	4.0(2)	0.7(2)	0.5(2)	1.4(2)
C(3)	0.9316(5)	0.1952(4)	0.6713(5)	6.1(2)	3.7(2)	3.8(2)	0.4(2)	1.3(2)	0.5(2)
C(4)	0.8808(4)	0.2107(4)	0.5427(4)	4.6(2)	2.9(2)	3.6(2)	0.9(1)	1.1(1)	0.5(1)
C(5)	1.0458(4)	0.4331(4)	0.3428(5)	5.7(2)	2.9(2)	4.6(2)	1.3(1)	2.6(1)	1.1(1)
C(6)	1.1021(4)	0.2859(4)	0.4418(4)	5.1(2)	3.9(2)	3.9(2)	1.7(1)	1.9(1)	1.8(1)
C(7)	1.1823(4)	0.3682(4)	0.5520(5)	4.7(2)	4.0(2)	4.6(2)	0.4(2)	0.8(2)	0.6(2)
C(8)	1.1843(5)	0.4822(4)	0.5522(5)	5.7(2)	3.7(2)	5.2(2)	0.8(2)	1.4(2)	0.8(2)
C(9)	0.5903(5)	0.1823(5)	0.3733(6)	6.6(2)	6.1(2)	5.6(3)	2.8(2)	1.9(2)	0.8(2)
C(10)	0.4977(5)	0.1855(6)	0.4295(6)	5.4(2)	8.0(3)	6.6(3)	2.2(2)	3.0(2)	1.6(2)
C(11)	0.4023(5)	0.0913(6)	0.3957(6)	5.6(2)	9.0(3)	5.9(3)	2.2(2)	2.6(2)	2.2(2)
C(12)	0.4006(5)	−0.0052(6)	0.3091(6)	4.3(2)	8.5(3)	6.1(3)	1.2(2)	1.4(2)	2.7(2)
C(13)	0.4960(4)	−0.0062(5)	0.2577(6)	3.8(2)	5.8(2)	5.3(2)	0.6(2)	0.8(2)	2.1(2)
C(14)	1.1032(4)	0.3159(4)	0.0140(5)	5.7(2)	5.2(2)	3.5(2)	1.0(2)	2.1(1)	1.4(2)
C(15)	1.2056(5)	0.3183(5)	−0.0216(6)	6.8(2)	6.5(3)	4.7(2)	1.4(2)	2.8(2)	1.0(2)
C(16)	1.2695(5)	0.2417(6)	0.0159(6)	5.3(2)	8.3(3)	4.8(2)	1.5(2)	2.2(2)	0.5(2)
C(17)	1.2269(5)	0.1630(6)	0.0854(6)	6.7(2)	8.6(3)	5.9(3)	3.9(2)	2.5(2)	1.6(2)
C(18)	1.1239(4)	0.1648(5)	0.1178(5)	6.4(2)	6.1(2)	5.5(2)	3.1(2)	3.2(2)	2.1(2)

Atom	x	y	z	B,Å^2	Atom	x	y	z	B,Å^2
C(101)	0.3206(8)	0.5816(9)	0.251(1)	10.9(3)	C(104)	0.5171(9)	0.5307(9)	0.211(1)	11.3(3)
C(102)	0.3676(10)	0.6360(9)	0.166(1)	11.8(3)	C(105)	0.4760(9)	0.4913(9)	0.289(1)	11.9(3)
C(103)	0.4746(10)	0.6095(11)	0.143(1)	13.9(4)	C(106)	0.3715(11)	0.5108(11)	0.310(1)	14.2(4)

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[a] The form of the anisotropic thermal parameter is: $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

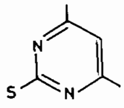
TABLE III. Bond Distances for $Mo_2O_4(SN_2C_4H_3)_2 \cdot 3NC_5H_5$.

Atoms	Distances (Å)	Atoms	Distances (Å)
Mo(1)–Mo(2)	2.576(1)	N(5)–C(9)	1.348(6)
–S(1)	2.567(1)	–C(13)	1.327(5)
–O(1)	1.956(3)	N(6)–C(14)	1.341(5)
–O(2)	1.684(3)	–C(18)	1.334(5)
–O(3)	1.947(2)	C(2)–C(3)	1.384(6)
–N(2)	2.310(3)	C(3)–C(4)	1.376(5)
–N(5)	2.278(3)	C(6)–C(7)	1.380(5)
Mo(2)–S(2)	2.565(1)	C(7)–C(8)	1.379(6)
–O(1)	1.961(3)	C(9)–C(10)	1.391(6)
–O(3)	1.927(2)	C(10)–C(11)	1.358(7)
–O(4)	1.679(3)	C(11)–C(12)	1.361(8)
–N(3)	2.295(3)	C(12)–C(13)	1.387(7)
–N(6)	2.271(3)	C(14)–C(15)	1.373(6)
S(1)–C(1)	1.726(4)	C(15)–C(16)	1.373(7)
S(2)–C(5)	1.729(4)	C(16)–C(17)	1.368(7)
N(1)–C(1)	1 351(5)	C(17)–C(18)	1.371(6)
–C(2)	1.335(5)		
N(2)–C(1)	1.342(4)		
–C(4)	1.347(4)		
N(3)–C(5)	1.362(5)		
–C(6)	1.357(5)		
N(4)–C(5)	1.340(5)		
–C(8)	1.338(6)		

TABLE IV. Bond Angles for $Mo_2O_4(SN_2C_4H_3)_2 \cdot 3NC_5H_5$.

Atoms	Angle (deg.)
Mo(2)–Mo(1)–S(1)	133.77(3)
–O(1)	48.97(7)
–O(2)	104.6(1)
–O(3)	47.99(7)
–N(2)	100.91(7)
–N(5)	133.45(9)
S(1)–Mo(1)–O(1)	148.73(8)
–O(2)	96.6(1)
–O(3)	86.59(7)
–N(2)	62.99(7)
–N(5)	87.30(9)
O(1)–Mo(1)–O(2)	113.2(1)
–O(3)	92.8(1)
–N(2)	85.7(1)
–N(5)	84.8(1)
O(2)–Mo(1)–O(3)	108.0(1)
–N(2)	154.3(1)
–N(5)	87.5(1)
O(3)–Mo(1)–N(2)	87.2(1)
–N(5)	163.9(1)
N(2)–Mo(1)–N(5)	76.7(1)
Mo(1)–S(1)–C(1)	82.6(1)
Mo(2)–S(2)–c(5)	82.9(1)
Mo(1)–O(1)–Mo(2)	82.2(1)
Mo(1)–O(3)–Mo(2)	83.37(9)
C(1)–N(1)–C(2)	116.0(3)
Mo(1)–N(2)–C(1)	102.0(2)
–C(4)	139.2(2)
C(1)–N(2)–C(4)	118.8(3)
Mo(2)–N(3)–C(5)	102.5(2)
–C(6)	139.2(2)
C(5)–N(3)–C(6)	118.2(3)
C(5)–N(4)–C(6)	116.2(3)
Mo(1)–N(5)–C(9)	120.6(3)
–C(13)	120.6(3)
C(9)–N(5)–C(13)	118.7(4)
Mo(2)–N(6)–C(14)	120.6(3)
–C(18)	121.6(3)
C(14)–N(6)–C(18)	117.7(4)
S(1)–C(1)–N(1)	123.4(2)
–N(2)	112.4(3)
N(1)–C(1)–N(2)	124.2(3)
N(1)–C(2)–C(3)	123.3(4)
C(2)–C(3)–C(4)	117.3(3)
C(3)–C(4)–N(2)	120.3(3)
Mo(1)–Mo(2)–S(2)	133.41(3)
–O(3)	48.63(7)
–O(4)	104.9(1)
–O(1)	48.79(7)
–N(3)	101.14(7)
–N(6)	132.97(8)
S(2)–Mo(2)–O(3)	148.11(8)
–O(4)	97.1(1)
–O(1)	85.58(8)
–N(3)	63.26(7)
–N(6)	87.91(9)
O(3)–Mo(2)–O(4)	113.4(1)
O(1)–Mo(2)–O(3)	93.2(1)
O(3)–Mo(2)–N(3)	84.9(1)
–N(6)	84.6(1)
O(4)–Mo(2)–O(1)	108.1(1)
–N(3)	154.0(1)
–N(6)	87.2(1)
–N(3)	88.3(1)
O(1)–Mo(2)–N(6)	164.6(1)
N(3)–Mo(2)–N(6)	75.7(1)
S(2)–C(5)–N(3)	111.3(3)
–N(4)	124.7(3)
N(3)–C(5)–N(4)	124.0(4)
N(3)–C(6)–C(7)	120.5(3)
C(6)–C(7)–C(8)	117.0(4)
C(7)–C(8)–N(4)	123.9(4)
N(5)–C(9)–C(10)	121.2(4)
C(9)–C(10)–C(11)	119.6(5)
C(10)–C(11)–C(12)	118.9(4)
C(11)–C(12)–C(13)	119.8(5)
C(12)–C(13)–N(5)	121.7(5)
N(6)–C(14)–C(15)	122.1(4)
C(14)–C(15)–C(16)	119.6(4)
C(15)–C(16)–C(17)	118.4(4)
C(16)–C(17)–C(18)	119.2(4)
C(17)–C(18)–N(6)	122.9(4)

with some previously reported compounds and reactions. The ligand, 2-thiopyrimidine, has previously [6] been reacted with $W(CO)_6$, but this gave a mononuclear product, containing no oxygen, of tungsten(IV), *viz.*, $W(SN_2C_4H_3)_4$. The reaction of $Mo(CO)_6$ with 2-thiopyrimidine has not yet been examined. When $Mo_2(O_2CCH_3)_4$ was treated with solutions of the sodium salts of the anions *3* and *4*, the products [7, 8] were the anticipated dinuclear ones, Mo_2L_4, in which the Mo–Mo quadruple bond is retained.



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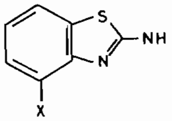

4 X = CH_3, Cl

In preparing the present compound, a green, insoluble solid was first obtained. We have not determined the formula or structure of that material. Analyses for C, N and H are reproducible and consistent with these elements being present in the 4:2:3 atom ratio required by the formula of the ligand, but their absolute values, 27.7, 15.8 and 1.9% respectively, are lower than those required by the formula $Mo_2(SN_2C_4H_3)_4$, *viz.*, 30.2, 17.6 and 1.89%, respectively. An infrared spectrum showed no bands indicative of Mo=O groups. Whatever the green substance may be, it is evidently quickly oxidized when its pyridine solution is exposed to air, thus producing the compound we have structurally characterized.

The structure found here is generally similar to those of most other compounds containing $Mo_2O_4^{2+}$ central units [5]. The first such structure [9] was recognized only rather recently, namely in 1965, and, subsequently, at least four others have been reported [5]. It is typical of all these structures to have an Mo–Mo distance in the range 2.54 to 2.58 Å and for the central $Mo(\mu\text{-}O)_2Mo$ ring to be strongly puckered with the closest distance between the non-intersecting O···O and Mo···Mo lines in the range of 0.30–0.36 Å· This puckering is presumably a means of allowing the metal atoms to approach more closely and thus a metal–metal bond can be formed without appreciable loss of Mo–O bond strength.

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Supplementary Material Available

A table of structure factors (15 pages).

References

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