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Synthesis and structural characterization of a binuclear Mo(V)–oxo complex which contains both thiolate and tertiary phosphine ligands, $[Mo_2O_4(2,4,6\text{-i-}Pr_3C_6H_2S)_2(PPh_3)_2]$

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Abstract

The reaction of $[MoCl_4(PPh_3)_2]$ with $2,4,6\text{-i-}Pr_3C_6H_2SH$ (TIPTH) in CH_2Cl_2, followed by introduction of an excess of O_2, yields the binuclear Mo(V) complex, $[Mo_2O_4(2,4,6\text{-i-}Pr_3C_6H_2S)_2(PPh_3)_2]$. An X-ray diffraction study of this complex revealed the presence of the common $[Mo_2O_4]^{2+}$ core, with each Mo(V) center additionally coordinated to the phosphorus donor of a triphenylphosphine and to the sulfur donor of a terminally ligated TIPT group. Crystal data for $[Mo_2O_4(2,4,6\text{-i-}Pr_3C_6H_2S)_2]$: orthorhombic space group *Pccn*, $a = 29.772(4)$, $b = 22.193(4)$, $c = 19.016(3)$ Å, $V = 12564.6(11)$ Å^3, $D_{calc} = 1.32$ g cm^{-1}, $Z = 8$. Structure solution and refinement based on 1279 reflections (Mo Kα, $\lambda = 0.71073$ Å, $2° \leq 2\theta \leq 45°$) converged at a conventional discrepancy value of 0.063.

Introduction

The chemistry of high-valent molybdenum–oxo complexes has received significant contemporary attention by virtue of the potential applications of these complexes as oxidation catalysts and as oxygen transfer agents [1, 2]. Molybdenum-mediated oxygen atom transfer reactions have frequently been studied in the form of atom transfer from Mo(VI) to tertiary phosphines [3–5], illustrated by reaction (1). Oxo transfer is accompanied by the formation of a

$$L_nMo^{VI}O_2 + PPh_3 \rightleftharpoons L_nMo^{IV}O + Ph_3PO \tag{1}$$

μ-oxo dimer in reaction (2) [1, 6], which occurs unless sterically encumbered ligands are present.

$$L_nMo^{VI}O_2 + L_nMo^{IV}O \rightleftharpoons [Mo_2O_3L_{2n}] \tag{2}$$

Since tertiary phosphine ligands have been used primarily in oxo-transfer reactions or in the synthesis of low-valent organometallic complexes of molybdenum, examples of mixed oxo–phosphine complexes of high valent molybdenum are rare and limited to Mo(IV) species, such as $[MoO\{S_2C_2(CN)_2\}(Ph_2PCH_2CH_2PPh_2)]$ [7], and $[MoOCl_2(PR_3)_3]$ [8, 9]. However, it has been demonstrated that ruthenium (IV)–oxo complexes containing tertiary phosphine ligands may be isolated if oxidation of the phosphine ligand is prevented by initial generation of a ruthenium–phosphine species, followed by oxidation to the phosphine–ruthenium(IV)–oxo complex [10]. By employing a similar strategy, we have isolated an unusual example of a binuclear phosphine–molybdenum(V)–oxo species $[Mo_2O_4(2,4,6\text{-i-}Pr_3C_6H_2S)_2(PPh_3)_2]$, in which the presence of the sterically encumbering thiolate ligand is also noteworthy.

Experimental

Materials

All chemicals and solvents were commercial products, unless otherwise specified. The ligand $2,4,6\text{-i-}Pr_3C_6H_2SH$ was prepared as described previously [11]. $[MoCl_4(PPh_3)_2]$ was synthesized by the standard method [12].

Preparation of $[Mo_2O_4(2,4,6\text{-i-}Pr_3C_6H_2S)_2(PPh_3)_2]$

Under an argon atmosphere, a suspension of $[MoCl_4(PPh_3)_2]$ (0.762 g, 1 mmol) in CH_2Cl_2 (20 ml)

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was added to a solution of 2,4,6-i-$Pr_3C_6H_2SH$ (0.944 g, 4 mmol) in CH_2CL_2 (10 ml). After stirring for 1 h, oxygen was introduced via syringe (5 ml), and the solution was stirred vigorously for an additional 2 h. The characteristic dark red–brown color of the molybdenum–thiolate species initially formed slowly discharged to yield a Chinese red solution. After concentration to *c*. 10 ml, the solution was carefully layered with diethylether (20 ml) and allowed to sit at 4 °C for four weeks, whereupon red crystals were collected in 10% yield. *Anal.* Calc. for $C_{66}H_{72}O_4P_2S_2Mo_2$: C, 63.5; H, 5.77. Found: C, 63.4; H, 5.82%.

X-ray crystallographic study

The details of the crystal data and experimental conditions for the structural study are summarized in Table 1. Atomic positional parameters are listed in Table 2. Full details of the crystallographic methods employed may be found in ref. 16. Selected bonds lengths and angles are given in Table 3.

TABLE 1. Summary of crystal data and experimental details for the structural study of $[Mo_2O_4(SC_6H_2Pr_3^i)_2(PPh_3)_2]$

Crystal parameters[a] *at* 23 °*C*	
a (Å)	29.772(4)
b (Å)	22.193(4)
c (Å)	19.016(3)
α (°)	90.0°
β (°)	90.0°
γ (°)	90.0°
V (Å^3)	12564.6(11)
Space group	*Pccn*
Z	8
D_{calc} (g cm^{-1})	1.32
D_{obs} (g cm^{-1})	1.34
Measurement of intensity data	
Crystal dimensions (mm)	0.12×0.14×0.11
Instrument	Nicolet R3m
Radiation	Mo Kα (λ=0.71073 Å)
Scan mode	coupled θ (crystal)–2θ(counter)
Scan rate (°/min)	variable: 5–30
Scan range	20–45 in 2θ
Scan length	from $[2\theta(K\alpha_1)-1.0]$ to $[2\theta(K\alpha_2)+1.0]$
Background measurement	stationary counter, stationary crystal at the beginning and end of each 2 scan; each taken for the time of the scan
Standards	3 collected every 197 reflections; no significant deviation over the 74 h of data collection
No. reflections collected	4421 in the quadrant ($+h$, $+k$, $+l$)
No. independent reflections used in solution	1279 unique reflections with $I_0 \geqslant 3\sigma(I_0)$
Reduction of intensity data and summary of structure solution and refinement[b]	
Data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion	
Absorption coefficient (cm^{-1})	5.46
Absorption correction	none
Structure solution	a three dimensional Patterson map yielded the positions of the Mo atoms; all non-hydrogen atoms were located on subsequent difference Fourier maps; hydrogen atoms were included as fixed contributors in the final refinement cycles
Atomic scattering factors[c]	neutral atomic scattering factors were used for all atoms
Anomalous dispersion[d]	applied to all non-hydrogen atoms
Final discrepancy factor[e]	
R	0.074
R_w	0.069
Goodness of fit[f]	1.54

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in ref. 13. [c] Ref. 14. [d] Ref. 15. [e] $R=\Sigma[|F_o|-|F_c|/\Sigma|F_o|]$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\delta^2(F_o)+g^*(F_o)^2$; $g=0.0001$. [f] $GOF=[\Sigma w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

TABLE 2. Atomic positional parameters ($\times 10^4$) and isotropic temperature factors ($Å^2 \times 10^3$) for [$Mo_2O_4(TIPT)_2(PPh_3)_2$]

Atom	x	y	z	U[a]
Mo(1)	887(1)	5423(2)	7061(2)	45(2)*
Mo(2)	961(1)	5313(1)	8414(2)	47(1)*
S(1)	911(4)	6298(4)	6342(4)	49(4)*
S(2)	1604(3)	5181(4)	9133(5)	53(5)*
P(1)	1409(4)	5031(4)	5987(5)	53(5)*
P(2)	732(3)	6079(4)	9470(5)	47(5)*
O(1)	451(7)	4984(8)	6813(10)	51(8)
O(2)	598(7)	4829(9)	8655(10)	63(8)
O(3)	731(5)	5953(8)	7835(11)	41(7)
O(4)	1308(6)	5034(8)	7635(11)	55(8)
C(1)	1956(12)	5347(19)	5892(18)	73(13)
C(2)	2331(12)	5015(15)	5870(16)	64(14)
C(3)	2784(12)	5269(17)	5801(16)	71(13)
C(4)	2824(15)	5920(20)	5775(20)	90(17)
C(5)	2449(12)	6206(15)	5772(15)	62(13)
C(6)	2033(13)	5984(18)	5835(16)	55(13)
C(11)	1112(13)	5177(17)	5157(19)	61(14)
C(12)	1390(12)	5190(15)	4519(20)	62(13)
C(13)	1209(13)	5287(17)	3881(20)	66(13)
C(14)	767(13)	5379(18)	3830(19)	66(14)
C(15)	511(14)	5313(19)	4412(22)	104(16)
C(16)	696(13)	5222(18)	5070(20)	64(14)
C(21)	1504(12)	4238(15)	6059(22)	58(13)
C(22)	1634(10)	3941(16)	6637(20)	56(13)
C(23)	1781(12)	3345(18)	6722(21)	98(16)
C(24)	1691(14)	3008(20)	6144(24)	104(19)
C(25)	1518(15)	3218(23)	5544(27)	144(22)
C(26)	1417(14)	3876(23)	5461(26)	126(20)
C(31)	774(12)	5771(19)	10345(20)	58(14)
C(32)	721(12)	5147(19)	10417(20)	66(15)
C(33)	712(12)	4890(20)	11055(23)	109(18)
C(34)	807(13)	5192(20)	11629(23)	109(18)
C(35)	929(14)	5795(17)	11582(21)	85(13)
C(36)	896(13)	6090(16)	10940(20)	75(13)
C(41)	1051(13)	6773(15)	9535(17)	54(12)
C(42)	840(12)	7294(15)	9630(16)	55(13)
C(43)	1056(13)	7843(18)	9672(17)	76(15)
C(44)	1538(12)	7842(17)	9696(17)	63(14)
C(45)	1751(11)	7321(15)	9615(17)	51(13)
C(46)	1483(12)	6807(15)	9557(17)	48(12)
C(51)	129(11)	6312(15)	9403(20)	50(12)
C(52)	−109(12)	6278(15)	10019(20)	67(14)
C(53)	−536(12)	6509(14)	9968(18)	44(13)
C(54)	−721(12)	6730(15)	9364(20)	77(15)
C(55)	−467(14)	6763(17)	8777(20)	91(16)
C(56)	−1(11)	6569(13)	8801(17)	40(12)
C(61)	619(11)	6896(14)	6758(17)	45(11)
C(62)	862(12)	7330(14)	7177(19)	57(11)
C(63)	625(12)	7788(15)	7455(18)	87(15)
C(64)	184(11)	7864(14)	7334(18)	47(12)
C(65)	−93(11)	7445(16)	7010(18)	72(13)
C(66)	147(12)	6951(15)	6689(18)	53(12)
C(71)	1349(12)	7286(15)	7176(26)	65(13)
C(72)	1538(16)	7550(25)	7824(21)	152(23)
C(73)	1612(11)	7584(17)	6596(16)	59(13)
C(74)	−29(17)	8414(23)	7724(31)	119(18)
C(75)	−115(13)	8363(18)	8453(18)	111(17)
C(76)	−498(15)	8518(21)	7359(28)	191(26)
C(77)	−113(13)	6521(17)	6280(22)	60(14)
C(78)	−291(15)	6771(20)	5603(22)	161(22)
C(79)	−451(13)	6240(20)	6696(24)	146(20)
C(81)	2037(10)	4820(14)	8670(15)	33(11)
C(82)	2351(10)	5097(12)	8285(16)	33(11)
C(83)	2738(12)	4837(16)	7943(18)	74(14)
C(84)	2756(12)	4209(18)	7976(20)	77(14)
C(85)	2445(12)	3878(15)	8383(18)	59(12)
C(86)	2067(12)	4171(18)	8704(19)	66(14)
C(91)	2314(12)	5806(18)	8208(24)	109(17)
C(92)	2516(15)	6073(17)	7572(19)	126(19)
C(93)	2583(12)	6078(15)	8794(15)	78(14)
C(94)	3216(15)	3926(23)	7687(30)	105(16)
C(95)	3267(16)	3283(18)	7992(28)	204(27)
C(96)	3086(16)	3851(21)	6918(21)	172(23)
C(97)	1785(14)	3817(18)	9161(23)	86(15)
C(98)	1620(13)	3272(21)	8734(24)	146(22)
C(99)	2008(15)	3590(22)	9855(20)	155(20)

[a] Starred items: *equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond lengths (Å) and angles (°) for [$Mo_2O_4(TIPT)_2(PPh_3)_2$]

Mo(1)–Mo(2)	2.595(4)
Mo(1)–O(1)	1.69(2)
Mo(1)–O(3)	1.94(2)
Mo(1)–O(4)	1.88(2)
Mo(1)–S(1)	2.38(1)
Mo(1)–P(1)	1.711(9)
Mo(2)–O(2)	1.60(2)
Mo(2)–O(3)	1.92(2)
Mo(2)–O(4)	1.91(2)
Mo(2)–S(2)	2.37(1)
Mo(2)–P(2)	2.718(8)
S(1)–Mo(1)–O(1)	109.6(7)
S(1)–Mo(1)–O(3)	87.1(6)
S(1)–Mo(1)–O(4)	133.8(6)
S(1)–Mo(1)–P(1)	79.1(4)
O(1)–M(1)–O(3)	112.2(8)
O(1)–Mo(1)–O(4)	114.2(9)
O(1)–Mo(1)–P(1)	92.6(6)
O(3)–Mo(1)–O(4)	89.9(8)
O(3)–Mo(1)–P(1)	154.6(6)
O(4)–Mo(1)–P(1)	84.7(6)
S(2)–Mo(2)–O(2)	107.4(8)
S(2)–Mo(2)–O(3)	135.2(6)
S(2)–Mo(2)–O(4)	88.3(6)
S(2)–Mo(2)–P(2)	81.6(4)
O(2)–Mo(2)–O(3)	114.9(9)
O(2)–Mo(2)–O(4)	111.9(9)
O(2)–Mo(2)–P(2)	92.2(6)
O(3)–Mo(2)–O(4)	89.3(8)
O(3)–Mo(2)–P(2)	82.6(6)
O(4)–Mo(2)–P(2)	155.8(6)

Results and discussion

The reaction of $[MoCl_4(PPh_3)_2]$ with 2,4,6-i-$Pr_3C_6H_2SH$ (TIPTH) in CH_2Cl_2 yields a dark red–brown solution from which a red powder may be isolated upon addition of diethyl ether. Although infrared spectroscopy of this material exhibited bands associated with Mo–CL stretch and the presence of both the phosphine and thiolate ligands, no consistent analytical results could be achieved, nor could the material be induced to crystallize. The identity of this material remains undetermined and is evidently a mixture of products. However, the solutions of this material reacted cleanly with molecular oxygen to yield the title complex.

The synthesis of $[Mo_2O_4(TIPT)_2(PPh_3)_2]$ relies upon the initial generation of a molybdenum–thiolate–phosphine complex in solution, so as to avoid oxidation of the tertiary phosphine by a molybdenum–oxo moiety. Subsequent addition of molecular oxygen results in oxidation to the phosphine–molybdenum(V)–oxo species.

Although the presence of thiolate ligands would be expected to favor reduced molybdenum centers, it has been demonstrated that sterically-hindered ligands of the TIPT family stabilize metal–thiolate coordination for metals in high oxidation states [17–19]. However, the isolation of a binuclear complex in the presence of such sterically demanding ligands as TIPT And PPh_3 was unanticipated in view of our previous experience with the TIPT family of ligands in the preparation of mononuclear species [20]. It is noteworthy that with thiophenol, the identical reaction conditions yield intractable materials.

As illustrated in the perspective view of the molecule presented in Fig. 1, the structure of $[Mo_2O_4(TIPT)_2(PPh_3)_2]$ consists of discrete binuclear units. Each molybdenum exhibits irregular five-coordinate geometry which may be loosely described as distorted square pyramidal. The basal plane about each molybdenum atom is generated by the two bridging oxo groups and the sulfur and phosphorous donors of the terminal TIPT and triphenylphosphine ligands, respectively, while the terminal oxo group occupies the apical position. The binuclear unit is generated by edge-sharing of the two square pyramids along O3–O4 vector.

The $[Mo_2O_4]^{2+}$ unit is a common feature in the structural chemistry of Mo(V) [21]. The short Mo–Mo distance of 2.595(4) Å is consistent with the geometric requirements of two edge-sharing square pyramidal units and with a degree of direct metal–metal interaction. The structural parameters within the $[Mo_2O_4]^{2+}$ unit are similar to those observed for previously reported examples of this structural type, as shown in Table 4. The *syn-endo* configuration of the terminal oxo groups is also a structural characteristic common to this unit.

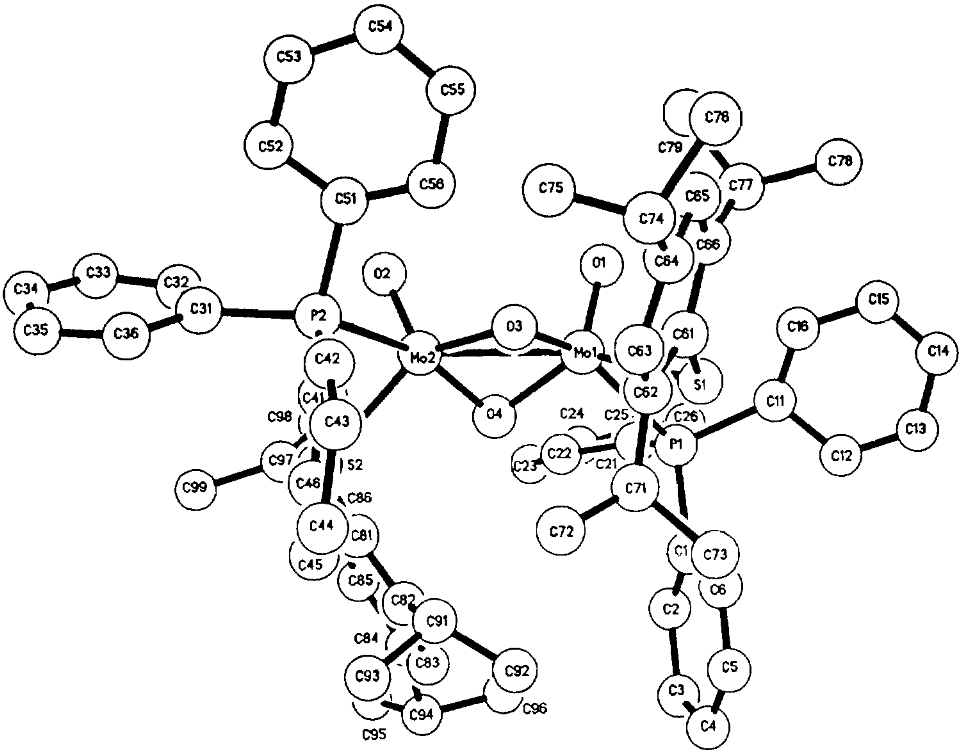

Fig. 1. ORTEP view of the structure of $[Mo_2O_4(TIPT)_2(PPh_3)_2]$, showing the atom-labelling scheme.

TABLE 4. Selected structural parameters for complexes with the $[Mo_2O_4]^{2+}$ core with sulfur-containing ligands[a]

Complex	Geometry	Mo–Mo	Mo–O_t	Mo–O_b	Mo–L(L)[b]	Mo displacement[c]	Reference
$Na_2[Mo_2O_4(cys)_2]$	octahedral	2.569(2)	1.71(2)	1.93(2)	2.490(6)(S) 2.23(2)(N) 2.30(2)(O)	0.38	22
$[Mo_2O_4(Et\text{-}cys)_2]$	trigonal bipyramidal	2.562(3)	1.66(2)	1.93(2)	2.380(8)(S) 2.219(3)(N)		23
$[Mo_2O_4(S_2CNEt_2)_2]$	square pyramidal	2.580(1)	1.678(2)	1.941(1)	2.445(3)(S)	0.74	24
$(R_4N)_2[Mo_2O_4(SPh)_4]$	square pyramidal	2.677(2)	1.674(9)	1.932(9)	2.451(4)(S)	0.70	25
$[Mo_2O_4(C_9H_{22}N_2S_2)_2]$	square pyramidal	2.623(1)	1.68(1)	1.946(9)	2.439(4)(S)	0.71	26
$[Mo_2O_4(TIPT)_2(PPh_3)_2]$	distorted square pyramidal	2.595(4)	1.64(2)	1.93(1)	2.373(8)(S) 2.725(8)(P)	0.64	this work

[a] Abbreviations: O_t, terminal oxo group; O_b, bridging oxo group. [b] The ligand donor group in parentheses, (L). [c] Distance from Mo to the ligand O–P–S–O plane.

However, the significant distortion of the molybdenum coordination spheres of $[Mo_2O_4(TIPT)_2(PPh_3)_2]$ from idealized square pyramidal geometry is unusual. This distortion is illustrated by the deviations of Mo1 and Mo2 from the S1–P1–O3–O4 and S2–P2–O3–O4 planes, respectively, of 0.63 Å and by the S1–Mo1–O4 and S2–Mo2–O3 angles of 133.8(6) and 135.2(6)°, respectively. An analysis of the basal 'planes', S1–P1–O3–O4 and S2–P2–O3–O4, reveals considerable distortion as illustrated by the dihedral angles between the edge-sharing planes S1–P1–O3 and P1–O3–O4 of 18.9° and an angle of 18.8° between S2–P2–O3 and P2–O3–O4, whereas an idealized square pyramid requires coplanarity. This distortion may be a consequence of the severe steric constraints imposed by the bulky terminal ligands, triisopropylphenylthiolate and triphenylphosphine. The long Mo–P distances, 2.72 Å (av.), are consistent with the high degree of steric congestion about the molybdenum atoms.

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