

Novel oxo-bridged dinuclear molybdenum(II) complexes: reaction of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ with aromatic isocyanides. X-Ray crystal structures of $[\text{Mo}_2(\mu\text{-O})(\text{RNC})_{10}](\text{BF}_4)_2$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) and $[\text{Mo}(=\text{O})\text{F}(\text{RNC})_4](\text{BF}_4)$ ($\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$)[☆]

Toshiaki Igoshi, Tomoaki Tanase^{*}, Yasuhiro Yamamoto^{*}

Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274, Japan

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Abstract

Treatment of the dinuclear molybdenum complex $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ with aromatic isocyanides (RNC) gave an oxo-bridged dinuclear molybdenum(II) complex, $[\text{Mo}_2(\mu\text{-O})(\text{RNC})_{10}](\text{BF}_4)_2$ (**1**), and a mononuclear molybdenum(IV) complex, $[\text{Mo}(=\text{O})\text{F}(\text{RNC})_4](\text{BF}_4)$ (**2**) ($\text{R} = 2,6\text{-dimethylphenyl (Xyl)}$ or $2,4,6\text{-trimethylphenyl (Mes)}$), which were characterized by IR, electronic, ¹H and ¹⁹F NMR spectroscopy and X-ray crystallographic analyses. Complex **1a** ($\text{R} = \text{Xyl}$) crystallizes in the triclinic form, space group $P\bar{1}$, with $a = 13.431(5)$ Å, $b = 15.548(7)$ Å, $c = 12.616(5)$ Å, $\alpha = 111.74(3)^\circ$, $\beta = 92.80(3)^\circ$, $\gamma = 101.80(3)^\circ$ and $Z = 1$ ($R = 0.060$ and $R_w = 0.054$ for 2818 independent reflections with $I > 3\sigma(I)$). Complex **2b** ($\text{R} = \text{Mes}$) crystallizes in the triclinic form, space group $P\bar{1}$, with $a = 14.317(4)$ Å, $b = 16.16(1)$ Å, $c = 8.968(8)$ Å, $\alpha = 100.31(4)^\circ$, $\beta = 97.54(2)^\circ$, $\gamma = 91.69(4)^\circ$ and $Z = 2$ ($R = 0.059$ and $R_w = 0.059$ for 2225 independent reflections with $I > 3\sigma(I)$). Complex **1** consists of two molybdenum atoms bridged linearly by an oxygen atom. Each molybdenum atom is octahedrally coordinated by five isocyanides and an oxygen atom. Two equatorial planes, $\text{Mo}(\text{RNC})_4$, mutually adopt an eclipsed form. The Mo–O bond length is $1.876(2)$ Å and the Mo–O–Mo angle is constrained to 180° . Complex **2** has a distorted octahedral geometry, in which molybdenum atom is occupied by four isocyanides, O and F atoms.

Keywords: Molybdenum; Oxo-bridged dinuclear complexes; X-ray diffraction; Isocyanide; EHMO

1. Introduction

Multiple bonds between metal atoms of Group 6 have been known for many years and are still a topic of current interest. In particular, dinuclear tetracarboxylate complexes of $\text{M}_2(\text{O}_2\text{CCH}_3)_4$ ($\text{M} = \text{Cr, Mo, and W}$) that contain a $\sigma^2\pi^4\delta^2$ M–M quadruple bond have received considerable attention for their interesting structures, spectroscopic properties and reactivities [1]. However, the poor solubility of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ in organic solvents obstructed further development of their reactions with a number of organic molecules. Cotton et al. [2] and Pimblett and co-workers [3] independently reported the synthesis and characterization of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2-$

$(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ which is soluble in most polar organic solvents. We were interested in the reactivity of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$, because of its good solubility and easy access of organic molecules to the $[\text{Mo}_2]^{4+}$ center.

We report here the reaction of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ with aromatic isocyanides (RNC) to give a linear oxo-bridged dinuclear molybdenum(II) complex and a mononuclear molybdenum(IV) complex. In particular, the former compound is the first example of a μ -oxo dimolybdenum complex involving a divalent Mo center.

2. Experimental

All manipulations were carried out under a nitrogen atmosphere. Solvents were distilled over lithium aluminum hydride. H_2^{18}O (Aldrich) was used as received.

[☆] Studies on the interaction of isocyanide with transition metal complexes, Part 41. For Part 40, see Y. Yamamoto, T. Tanase and R. Sugano, *J. Organomet. Chem.*, **486** (1995) 21–29.

^{*} Corresponding authors.

$[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ (**3**) and isocyanides (**4**) were prepared by known methods. Infrared and electronic absorption spectra were recorded on Jasco FT/IR 5300 and Ubest-30 spectrometers, respectively. ^1H NMR spectroscopy was carried out on a JEOL EX-400 instrument at 400 MHz in CDCl_3 , using tetramethylsilane (TMS) as an internal reference. ^{19}F NMR spectroscopy was carried out on a Bruker AC250 instrument at 235 MHz in CDCl_3 , using CFCl_3 as an external reference.

2.1. Preparation of $[\text{Mo}_2(\mu\text{-O})(\text{RNC})_{10}](\text{BF}_4)_2$ (**1**) and $[\text{Mo}(=\text{O})\text{F}(\text{RNC})_4]\text{BF}_4$ (**2**)

To a solution of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ (300 mg, 0.4 mmol) and 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$ (XylNC) (539 mg, 4.0 mmol) in 40 ml of THF was added a drop of water and the mixture was stirred at room temperature for 12 h. The solvent was removed by evaporation to dryness under reduced pressure. The residue was washed with diethyl ether and extracted with CHCl_3 . The solution was concentrated to ca. 5 ml and addition of diethyl ether gave green crystals of $[\text{Mo}_2(\mu\text{-O})(\text{XylNC})_{10}](\text{BF}_4)_2 \cdot 2\text{CHCl}_3$ (**1a**), yield 30%. Anal. Calcd. for $\text{C}_{90}\text{H}_{90}\text{B}_2\text{F}_8\text{Mo}_2\text{N}_{10}\text{O} \cdot 2\text{CHCl}_3$: C, 57.19; H, 4.80; N, 7.25. Found: C, 56.33; H, 4.79; N, 7.20%. IR (Nujol): $\nu_{\text{N}=\text{C}}$ 2062 cm^{-1} . UV–Vis (CHCl_3): λ_{max} (log ϵ) 967 (2.71), 831 (2.66), 565 (5.05), 328 (4.71) nm. ^1H NMR (CDCl_3): δ 2.07, 2.37 (s, *o*- CH_3), 7.03–7.16 (m, Ar).

In the preparation of **1a**, careful crystallization of the mother liquor gave yellow crystals of $[\text{Mo}(=\text{O})\text{F}(\text{XylNC})_4]\text{BF}_4$ (**2a**), yield 18%.

Anal. Calcd. for $\text{C}_{36}\text{H}_{36}\text{BF}_5\text{MoN}_4\text{O}$: C, 58.24; H, 4.89; N, 7.55. Found: C, 57.16; H, 4.56; N, 7.31%. IR (Nujol): $\nu_{\text{N}=\text{C}}$ 2170; $\nu_{\text{Mo}=\text{O}}$ 949 cm^{-1} . UV–Vis (CHCl_3): λ_{max} (log ϵ): 276 (4.72) nm. ^1H NMR (CDCl_3): δ 2.59 (s, *o*- CH_3), 7.29–7.44 (m, Ar). ^{19}F NMR (CDCl_3): δ -121.62 (s, Mo–F), -155.12 (s, $^{10}\text{BF}_4$), -155.17 (s, $^{11}\text{BF}_4$).

A similar procedure except using 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{NC}$ (MesNC) gave green crystals of $[\text{Mo}_2(\mu\text{-O})(\text{MesNC})_{10}](\text{BF}_4)_2$ (**1b**) and yellow crystals of $[\text{Mo}(=\text{O})\text{F}(\text{MesNC})_4]\text{BF}_4$ (**2b**). **1b**: yield 33%. Anal. Calcd. for $\text{C}_{100}\text{H}_{111}\text{B}_2\text{F}_8\text{Mo}_2\text{N}_{10}\text{O}$: C, 65.47; H, 6.10; N, 7.64. Found: C, 65.47; H, 5.50; N, 7.42%. IR (Nujol): $\nu_{\text{N}=\text{C}}$ 2066 cm^{-1} . UV–Vis (CHCl_3): λ_{max} (log ϵ) 965 (2.63), 830 (2.55), 568 (5.04), 330 (4.75) nm. ^1H NMR (CDCl_3): δ 2.00, 2.30 (s, *o*- CH_3), 2.18, 2.28 (s, *p*- CH_3), 6.76, 6.80 (s, *m*-H). **2b**: yield 16%. Anal. Calcd. for $\text{C}_{40}\text{H}_{44}\text{BF}_5\text{MoN}_4\text{O}$: C, 60.16; H, 5.55; N, 7.02. Found: C, 60.16; H, 5.40; N, 6.82%. IR (Nujol): $\nu_{\text{N}=\text{C}}$ 2193, 2162; $\nu_{\text{Mo}=\text{O}}$ 947 cm^{-1} . UV–Vis (CHCl_3): λ_{max} (log ϵ) 484 (2.64), 284 (4.74) nm. ^1H NMR (CDCl_3): δ 2.37 (s, *p*- CH_3), 2.52 (s, *o*- CH_3), 7.08 (s, *m*-H). ^{19}F NMR (CDCl_3): δ -122.44 (s, Mo–F), -155.53 (s, $^{10}\text{BF}_4$), -155.58 (s, $^{11}\text{BF}_4$).

2.2. X-ray crystallography

Crystal data and experimental conditions for **1a** and **2b** are listed in Table 1. Atomic positional parameters are listed in Tables 2 and 3. Green (**1a**) and yellow (**2b**) crystals sealed into a 0.7 mm o.d. glass capillary were used in the intensity data collection on a Rigaku AFC5S

Table 1
Crystallographic and experimental data for **1a** and **2b**

Parameter	1a	2b
Formula	$\text{C}_{92}\text{H}_{92}\text{N}_{10}\text{Mo}_2\text{Cl}_6\text{F}_8\text{OB}_2$	$\text{C}_{40}\text{H}_{44}\text{N}_4\text{BF}_5\text{MoO}$
<i>M</i>	1932.01	798.56
Crystallographic system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	13.431(5)	14.317(4)
<i>b</i> (Å)	15.548(7)	16.16(1)
<i>c</i> (Å)	12.616(5)	8.968(2)
α (°)	111.74(3)	100.31(4)
β (°)	92.80(3)	97.54(2)
γ (°)	101.80(3)	91.69(4)
<i>V</i> (Å ³)	2373(2)	2021(3)
<i>Z</i>	1	2
<i>T</i> (°C)	23	23
<i>D</i> _{calcd.} (g cm ⁻³)	1.352	1.312
μ (Mo K α) (cm ⁻¹)	4.91	3.71
No. of unique data	2818 (<i>I</i> > 3 σ (<i>I</i>))	2225 (<i>I</i> > 3 σ (<i>I</i>))
No. of parameters	547	469
<i>R</i> ^a	0.060	0.059
<i>R</i> _w ^b	0.054	0.059

^a $R = \sum \|F_o| - |F_c| \| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

four-circle automated diffractometer with Mo K α (0.7107 Å) radiation. Three standard reflections were monitored every 150 reflections and showed no systematic decrease in intensity. Totals of 8741 reflections (**1a**) and of 5252 reflections (**2b**) were measured and intensi-

Table 2

Positional and thermal parameters for non-hydrogen atoms of the complex cation of **1a**

Atom	x	y	z	B_{eq}^a
Mo(1)	0.0408(1)	0.11869(7)	0.12405(9)	2.44(4)
O(1)	0	0	0	2.4(4)
N(1)	−0.0579(7)	0.0108(6)	0.2863(7)	3.5(5)
N(2)	−0.1644(8)	0.1958(6)	0.1023(7)	3.8(4)
N(3)	0.1634(8)	0.2162(6)	−0.0385(9)	4.2(5)
N(4)	0.2602(8)	0.0954(6)	0.2204(8)	3.7(4)
N(5)	0.0787(8)	0.3163(7)	0.365(1)	4.5(5)
C(1)	−0.0236(9)	0.0521(7)	0.2322(9)	2.9(5)
C(2)	−0.093(1)	0.1636(8)	0.103(1)	3.5(5)
C(3)	0.117(1)	0.1830(7)	0.020(1)	3.2(5)
C(4)	0.185(1)	0.0990(7)	0.1780(9)	3.3(5)
C(5)	0.073(1)	0.2523(8)	0.278(1)	3.4(5)
C(11)	−0.077(1)	−0.0507(8)	0.3451(9)	3.5(5)
C(12)	−0.007(1)	−0.1065(8)	0.342(1)	3.7(5)
C(13)	−0.026(1)	−0.170(1)	0.398(1)	5.9(7)
C(14)	−0.112(1)	−0.171(1)	0.456(1)	6.5(8)
C(15)	−0.177(1)	−0.114(1)	0.460(1)	5.4(6)
C(16)	−0.161(1)	−0.0529(8)	0.403(1)	4.0(5)
C(17)	−0.234(1)	0.008(1)	0.408(1)	6.1(6)
C(18)	0.080(1)	−0.1025(8)	0.278(1)	5.5(6)
C(21)	−0.243(1)	0.243(1)	0.103(1)	4.5(6)
C(22)	−0.329(2)	0.220(1)	0.151(1)	7.0(8)
C(23)	−0.406(2)	0.265(2)	0.148(2)	11(1)
C(24)	−0.392(2)	0.331(2)	0.099(2)	13(2)
C(25)	−0.307(2)	0.356(1)	0.051(2)	10(1)
C(26)	−0.227(1)	0.311(1)	0.052(1)	6.2(7)
C(27)	−0.135(1)	0.331(1)	−0.001(1)	8.1(8)
C(28)	−0.343(1)	0.145(1)	0.198(1)	10(1)
C(31)	0.234(1)	0.248(1)	−0.104(1)	4.3(6)
C(32)	0.217(1)	0.314(1)	−0.145(1)	6.3(8)
C(33)	0.291(2)	0.340(1)	−0.209(2)	9(1)
C(34)	0.374(2)	0.303(2)	−0.227(2)	10(1)
C(35)	0.387(1)	0.238(1)	−0.181(1)	8.2(9)
C(36)	0.319(1)	0.207(1)	−0.119(1)	6.0(7)
C(37)	0.337(1)	0.138(1)	−0.069(1)	6.9(9)
C(38)	0.131(1)	0.357(1)	−0.119(1)	8.5(9)
C(41)	0.348(1)	0.0930(9)	0.286(1)	3.8(5)
C(42)	0.380(1)	0.0098(9)	0.262(1)	4.4(6)
C(43)	0.460(1)	0.010(1)	0.334(1)	5.9(6)
C(44)	0.507(1)	0.093(1)	0.426(1)	6.0(6)
C(45)	0.475(1)	0.174(1)	0.447(1)	5.5(6)
C(46)	0.395(1)	0.1776(9)	0.379(1)	4.6(6)
C(47)	0.358(1)	0.2671(8)	0.404(1)	6.9(6)
C(48)	0.328(1)	−0.0775(9)	0.160(1)	6.6(6)
C(51)	0.066(1)	0.3808(8)	0.476(1)	4.3(6)
C(52)	0.151(1)	0.4549(9)	0.540(1)	5.5(7)
C(53)	0.131(1)	0.512(1)	0.650(1)	6.6(8)
C(54)	0.037(2)	0.494(1)	0.685(1)	7.1(8)
C(55)	−0.043(1)	0.423(1)	0.617(1)	6.6(7)
C(56)	−0.031(1)	0.3617(8)	0.507(1)	4.4(6)
C(57)	−0.117(1)	0.2834(8)	0.429(1)	5.7(6)
C(58)	0.251(1)	0.477(1)	0.502(1)	7.5(7)

Estimated standard deviations are given in parentheses.

$$^a B_{eq} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* b_j^* a_i a_j.$$

Table 3

Positional and thermal parameters for non-hydrogen atoms of the complex cation of **2b**

Atom	x	y	z	B_{eq}^a
Mo(1)	0.2082(1)	0.23872(8)	0.1961(2)	3.71(6)
F(1)	0.2864(5)	0.2244(4)	0.3728(8)	5.0(4)
O(1)	0.1366(6)	0.2612(5)	0.0371(9)	4.1(4)
N(1)	0.3294(8)	0.0958(7)	−0.003(1)	4.1(6)
N(2)	0.0593(8)	0.0913(7)	0.256(1)	4.1(6)
N(3)	0.1276(7)	0.3862(7)	0.445(1)	3.8(5)
N(4)	0.3671(8)	0.3898(7)	0.196(1)	4.0(6)
C(1)	0.286(1)	0.1452(8)	0.064(2)	3.8(7)
C(2)	0.111(1)	0.1426(8)	0.233(2)	3.9(7)
C(3)	0.148(1)	0.3329(9)	0.352(2)	4.1(7)
C(4)	0.310(1)	0.3356(9)	0.184(2)	4.2(8)
C(11)	0.3819(9)	0.0434(8)	−0.094(1)	3.2(6)
C(12)	0.458(1)	0.0787(9)	−0.146(1)	3.9(7)
C(13)	0.504(1)	0.023(1)	−0.245(2)	5.0(8)
C(14)	0.474(1)	−0.061(1)	−0.292(2)	5.2(8)
C(15)	0.400(1)	−0.0907(8)	−0.237(2)	5.3(8)
C(16)	0.352(1)	−0.0407(9)	−0.132(1)	4.1(7)
C(17)	0.487(1)	0.169(1)	−0.101(2)	7.1(9)
C(18)	0.272(1)	−0.077(1)	−0.069(2)	5.9(8)
C(19)	0.524(1)	−0.119(1)	−0.406(2)	9(1)
C(21)	−0.0111(9)	0.0352(8)	0.283(2)	2.9(6)
C(22)	−0.010(1)	−0.0493(9)	0.227(2)	3.7(7)
C(23)	−0.083(1)	−0.0989(8)	0.258(2)	4.0(7)
C(24)	−0.150(1)	−0.069(1)	0.342(2)	4.7(9)
C(25)	−0.146(1)	0.016(1)	0.401(1)	4.8(7)
C(26)	−0.078(1)	0.0712(8)	0.371(1)	3.9(6)
C(27)	0.065(1)	−0.0819(8)	0.136(2)	6.4(8)
C(28)	−0.074(1)	0.163(1)	0.432(2)	7.1(9)
C(29)	−0.226(1)	−0.128(1)	0.370(2)	9(1)
C(31)	0.1162(8)	0.4563(8)	0.557(1)	3.3(6)
C(32)	0.082(1)	0.4459(8)	0.689(2)	4.1(7)
C(33)	0.078(1)	0.519(1)	0.799(2)	5.1(8)
C(34)	0.105(1)	0.596(1)	0.776(2)	4.8(7)
C(35)	0.141(1)	0.6026(8)	0.640(2)	5.0(7)
C(36)	0.147(1)	0.5343(8)	0.531(2)	4.0(7)
C(37)	0.053(1)	0.360(1)	0.711(2)	7.0(9)
C(38)	0.185(1)	0.5435(8)	0.385(2)	5.5(7)
C(39)	0.099(1)	0.674(1)	0.898(2)	7.5(9)
C(41)	0.438(1)	0.4552(8)	0.213(2)	3.9(7)
C(42)	0.527(1)	0.4432(8)	0.292(2)	4.2(7)
C(43)	0.594(1)	0.511(1)	0.311(2)	5.5(8)
C(44)	0.574(1)	0.5830(9)	0.256(2)	4.6(8)
C(45)	0.487(1)	0.5912(8)	0.181(2)	4.0(7)
C(46)	0.416(1)	0.5278(9)	0.154(1)	3.8(9)
C(47)	0.546(1)	0.364(1)	0.353(2)	8(1)
C(48)	0.321(1)	0.5384(8)	0.067(1)	4.6(7)
C(49)	0.652(1)	0.653(1)	0.279(2)	8(1)

Estimated standard deviations are given in parentheses.

$$^a B_{eq} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* b_j^* a_i a_j.$$

ties were corrected for Lorenz–polarization effects. An absorption correction was applied by the Ψ scan method.

The structures were solved by direct methods with MITHRIL [5]. The molybdenum atom was located in the initial E map and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The O(1) atom of **1a** was located on an inversion center of the unit cell with an occupancy of 0.5. The coordinates of all hydrogen atoms except for those of the solvent

molecules were calculated at the ideal positions with a C–H distance of 0.95 Å. The structure was refined with the full-matrix least-squares techniques minimizing $\sum w(|F_o| - |F_c|)^2$. Final refinement with anisotropic thermal parameters for non-hydrogen atoms (hydrogen atoms were not refined) converged to $R = 0.060$ and $R_w = 0.054$ for **1a** and $R = 0.059$ and $R_w = 0.059$ for **2b**, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). Atomic scattering factors and values of f' and f'' for Mo, Cl, F, O, C, N and B were taken from Refs. [6] and [7]. A final difference Fourier synthesis showed peaks at heights up to 0.48 e Å⁻³ (**1a**) and 0.44 e Å⁻³ (**2b**), respectively. All calculations were carried out on a Digital VAX Station 3100 M38 with the TEXSAN–TEXRAY program system [8].

2.3. EHMO calculations

Extended Hückel molecular orbital (EHMO) calculations were carried out using the following program [9] and the parameters were taken from Refs. [10] and [11]. The Mo–C (axial), Mo–C (equatorial), Mo–O, C–N and N–H distances were set to 2.20, 2.10, 1.88, 1.16 and 1.05 Å respectively. The Mo–O–Mo, Mo–C–N and C–N–H bond angles were idealized to be linear. All O–Mo–C (equatorial) bond angles were idealized to 90°.

3. Results and discussion

3.1. Reaction of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ with Isocyanides

The reaction of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ with an excess of isocyanide in THF containing a drop of water at room temperature yielded two complexes (green and yellow); the former is formulated as $[\text{Mo}_2(\mu\text{-O})(\text{RNC})_{10}](\text{BF}_4)_2$ (**1a**, R = Xyl, 30%; **1b**, R = Mes, 33%) and the latter as $[\text{Mo}(=\text{O})\text{F}(\text{RNC})_4]\text{BF}_4$ (**2a**, R = Xyl, 18%; **2b**, R = Mes, 16%). Compounds **1** and **2** are sensitive to air. In the absence of a drop of water, compounds **1** and **2** were not obtained and the reaction led to uncharacterized oily compounds together with a small amount of the zerovalent molybdenum complex of isocyanide, $\text{Mo}(\text{RNC})_6$ [12]. The IR spectra of **1** showed a peak at 2062–2065 cm⁻¹, corresponding to the terminal isocyanide groups ($\nu_{\text{N}=\text{C}}$). The ¹H NMR spectra indicated the presence of two kinds of isocyanides with a 1:4 intensity ratio. The electronic absorption spectra showed a characteristic band centered at 565–568 nm which was assigned to the $n \rightarrow \pi^*$ transition of the Mo–O–Mo unit compared with those of Ru^{IV}–O–Ru^{IV} and Os^{IV}–O–Os^{IV} compounds, having an isoelectronic structure [13]. The IR spectra of **2**

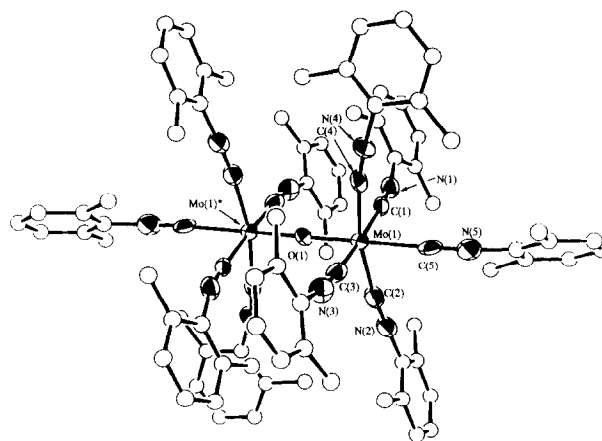


Fig. 1. Perspective drawing of the complex cation of **1a**, $[\text{Mo}_2(\mu\text{-O})(\text{XylNC})_{10}]^{2+}$.

showed peaks at 2162–2170 cm⁻¹ and ca. 950 cm⁻¹, assigned to the terminal isocyanide groups ($\nu_{\text{N}=\text{C}}$) and the terminal oxo group ($\nu_{\text{Mo}=\text{O}}$), respectively. The ¹H NMR spectra indicated the presence of one kind of isocyanide ligand, and the ¹⁹F NMR spectra exhibited the presence of coordinated fluorine atom at $\delta -122.62$ for **1a** and -122.44 for **2b**.

3.2. Structure of $[\text{Mo}_2(\mu\text{-O})(\text{XylNC})_{10}](\text{BF}_4)_2 \cdot 2\text{CHCl}_3$ (**1a**) and $[\text{Mo}(=\text{O})\text{F}(\text{MesNC})_4]\text{BF}_4$ (**2b**)

A perspective drawing of the complex cation of **1a** with the atomic numbering scheme is shown in Fig. 1 and bond distances and angles are given in Table 4. The cation of **1a** has a crystallographically imposed centrosymmetry and consists of two molybdenum atoms

Table 4
Some selected bond distances (Å) and angles (°) in **1a**

<i>Bond distances</i>			
Mo(1)–O(1)	1.876(2)	N(1)–C(1)	1.15(1)
Mo(1)–C(1)	2.12(1)	N(2)–C(2)	1.17(1)
Mo(1)–C(2)	2.10(1)	N(3)–C(3)	1.18(1)
Mo(1)–C(3)	2.11(1)	N(4)–C(4)	1.15(1)
Mo(1)–C(4)	2.14(1)	N(5)–C(5)	1.16(1)
Mo(1)–C(5)	2.20(1)		
<i>Bond angles</i>			
Mo(1)–O(1)–Mo(1)*	180.00	O(1)–Mo(1)–C(1)	88.4(3)
Mo(1)–C(1)–N(1)	175.9(9)	O(1)–Mo(1)–C(2)	95.9(3)
Mo(1)–C(2)–N(2)	173(1)	O(1)–Mo(1)–C(3)	91.9(3)
Mo(1)–C(3)–N(3)	177(1)	O(1)–Mo(1)–C(4)	95.9(3)
Mo(1)–C(4)–N(4)	171(1)	O(1)–Mo(1)–C(5)	173.5(3)
Mo(1)–C(5)–N(5)	170(1)	C(2)–Mo(1)–C(3)	93.0(4)
C(1)–Mo(1)–C(2)	91.9(4)	C(2)–Mo(1)–C(4)	168.1(4)
C(1)–Mo(1)–C(3)	175.1(5)	C(2)–Mo(1)–C(5)	80.9(4)
C(1)–Mo(1)–C(4)	86.9(4)	C(3)–Mo(1)–C(4)	88.2(4)
C(1)–Mo(1)–C(5)	86.0(4)	C(3)–Mo(1)–C(5)	93.9(4)
C(1)–N(1)–C(11)	165(1)	C(4)–Mo(1)–C(5)	87.2(4)
C(2)–N(2)–C(21)	174(1)	C(3)–N(3)–C(31)	169(1)
C(4)–N(4)–C(41)	173(1)	C(5)–N(5)–C(51)	167(1)

Estimated standard deviations are given in parentheses.

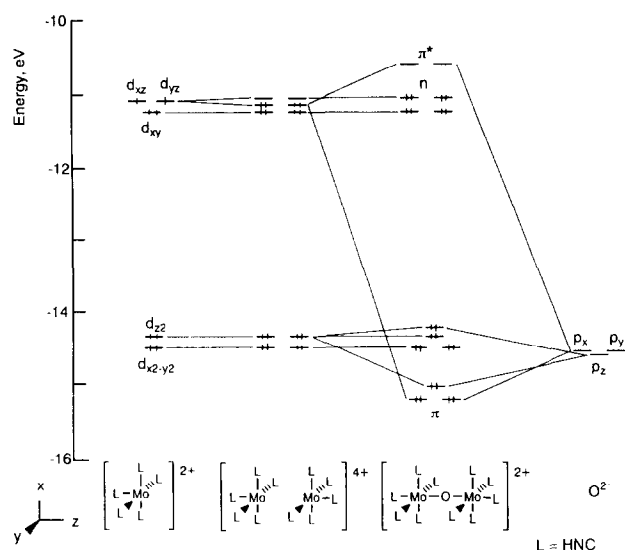
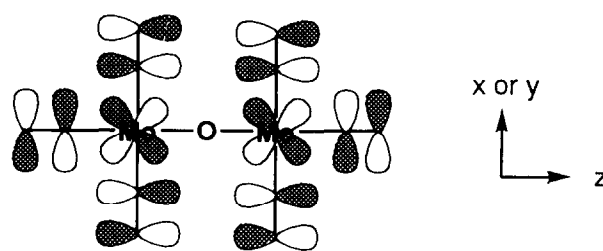


Fig. 2. Molecular orbital diagram of $[\text{Mo}_2(\mu\text{-O})(\text{HNC})_{10}]^{2+}$ (**3**).

bridged by an oxygen atom. Each molybdenum atom is octahedrally coordinated by five isocyanides and the bridging oxygen atom. Two equatorial planes, $\text{Mo}(\text{RNC})_4$, are mutually occupied with an eclipsed form. The most remarkable feature is that the apparent oxidation state of the molybdenum center is +2. There are several known d^4 – d^4 μ -oxo dinuclear complexes, such as $\text{Mn}_2(\mu\text{-O})(\text{Pc})_2(\text{py})_2$ and $\text{K}_4[\text{Ru}_2(\mu\text{-O})\text{Cl}_{10}]$, but μ -oxo dimolybdenum(II) complexes have not been obtained [14]. Although many μ -oxo complexes of molybdenum are known, they have oxidation states of +5 [15]. The μ -oxo complex $[\text{Mo}_2(\mu\text{-O})(\text{CH}_3\text{CN})_{10}](\text{BF}_4)_4$ [16], which is isostructural with complex **1** has been reported, but the oxidation number of the Mo atoms is +3. Compound **1** is isoelectronic with $\text{Ru}(\text{IV})$ and $\text{Os}(\text{IV})$ μ -oxo dimers and is the first isolated and characterized example of an oxo-bridged dimolybdenum(II) complex. The Mo–O–Mo angle is exactly 180° by



virtue of the centrosymmetry of the complex cation. The Mo–O bond length of 1.875(2) Å is slightly longer than that of $[\text{Mo}_2(\mu\text{-O})(\text{CH}_3\text{CN})_{10}](\text{BF}_4)_4$ (1.847(3) Å) [12], indicating that the $p_x \rightarrow d_x$ donating interaction between the O and the two Mo atoms is weaker than that in $[\text{Mo}_2(\mu\text{-O})(\text{CH}_3\text{CN})_{10}](\text{BF}_4)_2$. The Mo–C–N angles are in the range of 170 – 177° (average 173°) and the C–N–C angles are in the range 165 – 174° (average 169°). The C–N distances have an average value of 1.16 Å. The Mo–C bond length of the axial isocyanide (2.20(1) Å) is longer than those of the equatorial isocyanides (average 2.11 Å) because of the high *trans* effect of the oxygen atom.

In an attempt to elucidate an electronic structure of **1**, EHMO calculations were carried out on the model compound $[\text{Mo}_2(\mu\text{-O})(\text{HNC})_{10}]^{2+}$ (**3**). The interaction diagram for **3** in terms of $[(\text{HNC})_5\text{Mo} \cdots \text{Mo}(\text{HNC})_5]^{4+}$ and O^{2-} is illustrated in Fig. 2. The major interaction between two fragments is between the d_π orbitals of the Mo atoms and the p orbitals of the O atom. The LUMO consists of one (π^*) of these interactions. These interactions are usual in linear M–O–M complexes [17]. The HOMO of **3** is a set of nonbonding orbitals composed of d_{xz} and d_{yz} orbitals of the Mo atoms, which are stabilized by bonding interaction with π^* orbitals of HNC ligands as illustrated. This effect

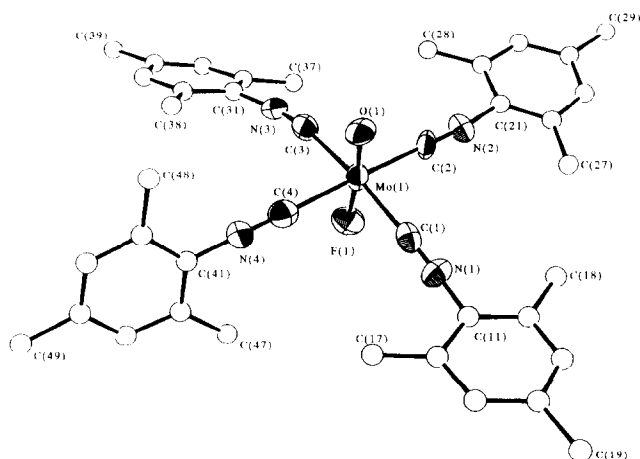


Fig. 3. Perspective drawing of the complex cation of **2b**, $[\text{Mo}(=\text{O})\text{F}(\text{MesNC})_4]^+$.

Table 5

Some selected bond distances (Å) and angles ($^\circ$) in **2b**

<i>Bond distances</i>			
Mo(1)–F(1)	1.871(8)	Mo(1)–O(1)	1.744(8)
Mo(1)–C(1)	2.17(1)	N(1)–C(1)	1.16(1)
Mo(1)–C(2)	2.15(1)	N(2)–C(2)	1.16(1)
Mo(1)–C(3)	2.16(1)	N(3)–C(3)	1.16(1)
Mo(1)–C(4)	2.14(1)	N(4)–C(4)	1.16(1)
<i>Bond angles</i>			
F(1)–Mo(1)–O(1)	175.1(4)	O(1)–Mo(1)–C(1)	94.9(4)
F(1)–Mo(1)–C(1)	88.5(4)	O(1)–Mo(1)–C(2)	94.2(5)
F(1)–Mo(1)–C(2)	89.2(4)	O(1)–Mo(1)–C(3)	92.7(5)
F(1)–Mo(1)–C(3)	83.8(4)	O(1)–Mo(1)–C(4)	91.1(4)
F(1)–Mo(1)–C(4)	85.3(5)	Mo(1)–C(1)–N(1)	178(1)
Mo(1)–C(2)–N(2)	179(1)	Mo(1)–C(3)–N(3)	171(1)
Mo(1)–C(4)–N(4)	172(1)	C(1)–N(1)–C(11)	174(1)
C(2)–N(2)–C(21)	174(1)	C(3)–N(3)–C(31)	172(1)
C(4)–N(4)–C(41)	178(2)		

Estimated standard deviations are given in parentheses.

led to the successful isolation of oxo-bridged complexes.

A perspective drawing of the complex cation of **2b** with the atomic numbering scheme is shown in Fig. 3 and some selected bond distances and angles are given in Table 5. The complex cation of **2b** is occupied by a terminal oxo group, a fluoride anion and four isocyanide molecules. The O and F atoms lie *trans* to each other and the four isocyanides complete an equatorial plane. The Mo–O bond length of 1.744(8) Å is a normal value for molybdenum–oxygen double bonds (Mo = O) [18]. The terminal isocyanides are bent towards the F atom with an average O–Mo–C_i angle of 93.2° and an average Fe–Mo–C_i angle of 86.7°. The origin of the F atom is responsible for BF₄[–] anions, because a similar reaction has been reported elsewhere [19].

3.3. Examinations by using ¹⁸O-enriched water

In order to elucidate the oxygen source of complexes **1** and **2**, reactions in the presence of enriched H₂¹⁸O were carried out. Complexes **1** and **2** could be prepared by the reaction of [Mo₂(O₂CCH₃)₂(CH₃CN)₆](BF₄)₂ with RNC in THF containing a drop of H₂¹⁸O. The presence of the ¹⁸O atom was confirmed by the IR spectra; the peak corresponding to ν (Mo = O) of **2** shifted to lower energy by ca. 50 cm^{–1} (949 → 901 cm^{–1} (**2a**) (903 cm^{–1} calculated value) and 947 → 899 cm^{–1} (**2b**) (901 cm^{–1} calculated value) but the shift of the ν_{as} (Mo–O–Mo) vibration could not be assigned precisely owing to its weak intensity. At present we consider that the oxygen atom in complexes **1** and **2** might arise from water, although we cannot rule out other possibilities.

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