Mono-Dithiolene Molybdenum(IV) Complexes of *cis*-1,2-Dicyano-1,2-ethylenedithiolate (mnt^{2-}): New Models for Molybdenum Enzymes

Hideki Sugimoto,*[a] Kazushi Siren,[b] Hiroshi Tsukube,[a] and Koji Tanaka[b]

Keywords: Molybdenum / Bioinorganic chemistry / Oxo ligands / S ligands / Oxidation

New mono-dithiolene molybdenum(IV) complexes of *cis*-1,2-dicyano-1,2-ethylenedithiolato [$(mnt)^{2-}$] have been synthesized as models for molybdenum enzymes, with 4,4′-di-*tert*-butyl-2,2′-bipyridine (Bu_2bpy) and, *N*,*N*′-tetraethylethylenediamine (Et_4en) as ancillary ligands, and characterized by IR, UV/Vis, elemental analysis, ESI-mass and electrochemical techniques. The temperature-dependent ^1H NMR spectra, recorded in CD_3CN solution, indicated that $[MoO(mnt)(Bu_2bpy)]$ (**1**) has a rigid structure but $[MoO(mnt)(Et_4en)]$ (**2**) showed dynamic conformational inversion processes involving the chelating ethylenediamine unit. The complexes exhibited different reactivities toward molecular oxygen: **1** gave a single oxo-bridged dimolybdenum dimer complex $[Mo_2O_3(mnt)_2(Bu_2bpy)_2]$ (**3**), while **2** did not react with O_2 and kept its mononuclear structure. Both complexes have almost the same redox potential for $Mo^{IV/V}$, and so the steric bulkiness and conformational dynamics were thought to cause this marked contrast. The obtained dimolybdenum complex **3** was also structurally characterized and investigated, and found to be a new dimolybdenum complex with one dithiolene per molybdenum. The crystal structure of the starting complex **4** was also reported.

Introduction

Molybdenum enzymes are widely distributed in nature and participate in catalytic cycles in biological reactions of the earth's carbon, nitrogen, and sulfur.[1] Crystallographic and X-ray absorption spectroscopic studies have revealed that most of these enzymes have active sites containing mononuclear molybdenum(IV) or -(VI) complexes coordinated by pterin-dithiolene cofactor ligands:[2] Formate dehydrogenase and dimethyl sulfoxide reductase have two dithiolene ligands, while sulfite oxidase, xanthin oxidase and nitrate reductase have one dithiolene per molybdenum center. Holm and co-workers and Ueyama and co-workers have presented mono- and des-oxo molybdenum(IV), and di- and mono-oxo molybdenum(VI) complexes with bis-dithiolene and -dithiolate ligands, which can be regarded as model complexes of the former enzymes.[3] Although other molybdenum complexes with two dithiolene ligands have been characterized,[4] only a few molybdenum complexes that contain one dithiolene ligand. Nicholas et al. isolated the mono-oxo complex of $[Mo^{IV}O(mnt)(Ph_2PCH_2CH_2PPh_2)]\cdot(CH_3)_2CO$ (mnt = *cis*-1,2-dicyano-1,2-ethylenedithiolate),[5] the first example of a structurally characterized molybdenum(IV) complex with mono-dithiolene ligands; however, its oxygen transfer properties were not elucidated. Enemark et al. reported several mono-dithiolene mono-oxo molybdenum complexes, $[Mo^VO(L)(3,5\text{-}Me_2Tp)]$ (L = $C_6H_4S_2$, $C_7H_6S_2$, $C_2H_2S_2$, Me_2Tp = hydrotris(3,5-dimethylpyrazol-2-yl-borato),[6] in which the molybdenum centers were in a +5 oxidation state and their hexacoordinate structures provided no open site for substrate binding. More recently, Holm et al. have presented a series of mono-dithiolene molybdenum(V), -(VI) complexes, mono-oxo derivatives $[MoOCl_2(L)]^-$, $[MoO(2\text{-}Ads)_2(L)]^-$ [L: dithiolene = $S_2C_2Me_2$ (1,2-dimethyl-1,2-ethylenedithiolate), bdt (1,2-benzenedithiolate)], $[MoO(SC_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3)_2(bdt)]^-$, $[MoOCl(SC_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3)_2(bdt)]^-$, and di-oxo derivatives $[MoO_2(L1)(bdt)]^-$ (L1 = $OSiPh_3$, $SC_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3$), as structural analogues for active sites of the sulfite oxidase enzyme family.[7] The mono-oxo molybdenum centers of these complexes also have an oxidation number of +5, as found in a resting form of native enzymes.

Here, we describe the synthesis and characterization of mono-dithiolene molybdenum(IV) complexes as new synthetic models for the active sites of sulfite oxidase, xanthin oxidase, and nitrate reductase. In addition to the mnt ligand, the ancillary ligands 4,4′-di-*tert*-butyl-2,2′-bipyridine (Bu_2bpy) provide σ-/π-bonding, and *N*,*N*′-tetraethylethylenediamine (Et_4en) give σ-donation character. Because most substrates in molybdenum enzyme reactions are neutral or negatively charged, the use of neutral Bu_2bpy and Et_4en

---

[a] Department of Chemistry, Graduate School of Science, Osaka City University,
Sumiyoshi-ku, Osaka 558−8585, Japan
Fax: (internat.) +81-6-6605-2522
E-mail: sugimoto@sci.osaka-cu.ac.jp
[b] Institute for Molecular Science,
Myodaiji, Okazaki 444−8585, Japan
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200200638

ligands offers different reactivities from those of previously reported model complexes having anionic ligands. Therefore, the present study offers new molybdenum models and also new insights into the reactivity of molybdenum enzymes.

Results and Discussion

Synthesis of Complexes

[MoO(mnt)(Bu$_2$bpy)] (**1**) was prepared by reacting [MoO$_2$Cl$_2$(Bu$_2$bpy)] (**4**) with Na$_2$mnt in CH$_3$OH. The IR spectrum of complex **1** shows strong absorptions at 2195 and 939 cm^{-1} assignable to ν(CN) of mnt and ν(Mo=O). Its ESI-mass signals centered at m/z = 561 in the presence of small amount of K$^+$ are consistent with the characteristic isotopic pattern of {[M] + K}$^+$. [MoO(mnt)(Et$_4$en)] (**2**) was obtained from the in situ reaction of MoO$_2$Cl$_2$ with Et$_4$en, and Na$_2$mnt in CH$_3$OH. The structure was similarly confirmed: IR: $\tilde{\nu}$ = 2194 and 906 cm^{-1}, ESI-mass m/z = 465 [M + K]$^+$. Elemental analysis data indicated that each complex had one oxo, one dithiolene, and one ancillary ligand (Figure 1). With Mo^{VI}, Na$_2$mnt, and ligands (1:1:1) the two complexes were obtained in 36 and 38% yield, respectively, suggesting that molybdenum(IV) formation is based on the reduction of molybdenum(VI) by the dithiolate of mnt^{2-}. In fact, the two-electron oxidized form of mnt^{2-}, [(mnt)$_2$]$^{2-}$ {[C$_2$(CN)$_2$SS−SSC$_2$(CN)$_2$]$^{2-}$}, was isolated from the filtrate (Figure S1 in the Supporting Information; see also the footnote on the first page of this article). Thus, we changed the ratio Mo^{VI}:Na$_2$mnt:ligands to 1:2:1, and improved the yield of [**1**] (56%). However, that of [**2**] was not improved under similar conditions and only a blue−green solution that was identical with [Mo(mnt)$_3$]$^{2-}$ was obtained.

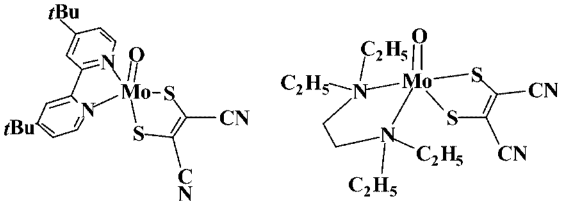


Figure 1. Structures of complexes **1** and **2**

Solution Structures of [MoO(Bu$_2$bpy)(mnt)] (1) and [MoO(Et$_4$en)(mnt)] (2): ^{1}H NMR Studies

Sharp ^{1}H NMR signals of [MoO(Bu$_2$bpy)(mnt)] (**1**) appeared in the region characteristic of diamagnetic molybdenum(IV)-d^2 complexes in CD$_3$CN: The signals for bipyridyl and butyl protons were observed at δ = 8.61, 8.44 and 7.68, and 1.42 ppm, respectively. Similarly, for [MoO(Et$_4$en)(mnt)] (**2**) the ^{1}H NMR spectrum supported a diamagnetic molybdenum(IV) complex structure, and showed temperature-dependent ^{1}H NMR behavior in CD$_3$CN (Figure 2).

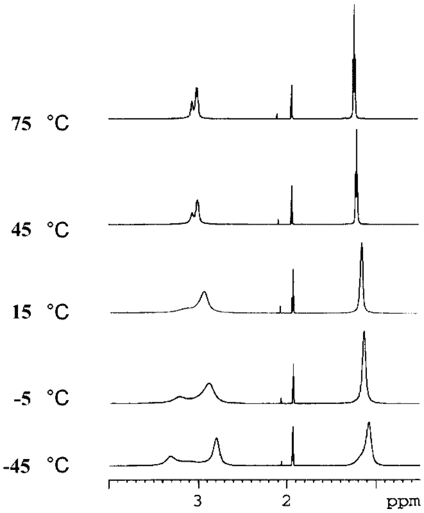
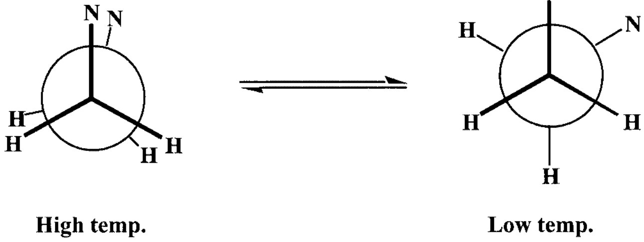


Figure 2. ^{1}H NMR spectra of [MoO(mnt)(Et$_4$en)] (**2**) in CD$_3$CN at various temperatures

At 75 °C, three signals appeared that were classified into two groups: Et and the C$_2$H$_4$ unit of ethylenediamine, based on their integration ratio. Methyl and methylene protons of the Et groups appeared at δ = 1.22 ppm (triplet) and δ = 3.00 ppm (broad doublet), while the C$_2$H$_4$ protons of ethylenediamine appeared as a broad singlet signal at δ = 3.05 ppm. These observations indicate that the four Et groups and two methylenes of C$_2$H$_4$ are equivalent within the ^{1}H NMR time scale. All the signals broadened as the temperature decreased from 75 to 15 °C. At lower temperatures, the broad signals for CH$_3$−CH$_2$−and for −CH$_2$−CH$_2$− protons appeared at δ = 1.08, 2.79, and δ = 3.20 ppm, respectively, though the signals for methyl and ethylene protons were still observed as broad signals. Such temperature-dependent spectral changes could be as due to a conformational inversion between pseudo-gauche and -steric strain conformations of the chelating ethylenediamine unit (Scheme 1), since each chemical shift (ppm) also moved. Similar conformational inversion has been reported in dimolybdenum and ditungsten complexes with ethylenediamine, [M$_2$(O)$_2$(μ-O)$_2$(μ-L)] (M = Mo, W; L = edta (ethylenediaminetetraacetato), tpen (*N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine)).[8]



Scheme 1. Proposed conformational change of **2** in CD$_3$CN (molybdenum center; [MoO(mnt)], is omitted for clarity

Reactivity of [MoO(Bu_2bpy)(mnt)] (1) and [MoO(Et_4en)(mnt)] (2)

Complex **1** shows interesting reactivity towards molecular oxygen in acetonitrile and acetone, giving the oxo-bridged dimolybdenum(V) complex [Mo_2O_3(Bu_2bpy)$_2$(mnt)$_2$] (**3**), the structure of which was confirmed by X-ray crystallography (Figure 5). Although the molecular oxygen is not a substrate in native molybdenum enzymes, it is a good oxygen donor. The reaction showed a color change, from yellow to deep blue-gray (Figure 3, a). The peaks centered at 492 and 590 nm intensified and the final spectrum exhibited a similar shape to that of mono-oxo bridged [Mo_2O_3(Bu_2bpy)$_2$(mnt)$_2$] (**3**) in CH_3CN, which was isolated independently as a crystalline powder. The ESI-MS spectrum recorded with the reaction solution is consistent with *m*/*z* = 1060 and the isotope pattern of dinuclear [Mo_2O_3(Bu_2bpy)$_2$(mnt)$_2$] (**3**). Since comproportionation, $Mo^{IV} + Mo^{VI} \rightarrow 2\ Mo^{V}$, is common in molybdenum chemistry,[9] the air oxidation process of **1** leading to **3** can be noted as Equation (1), in which the di-oxo molybdenum(VI) complex is a transient species.

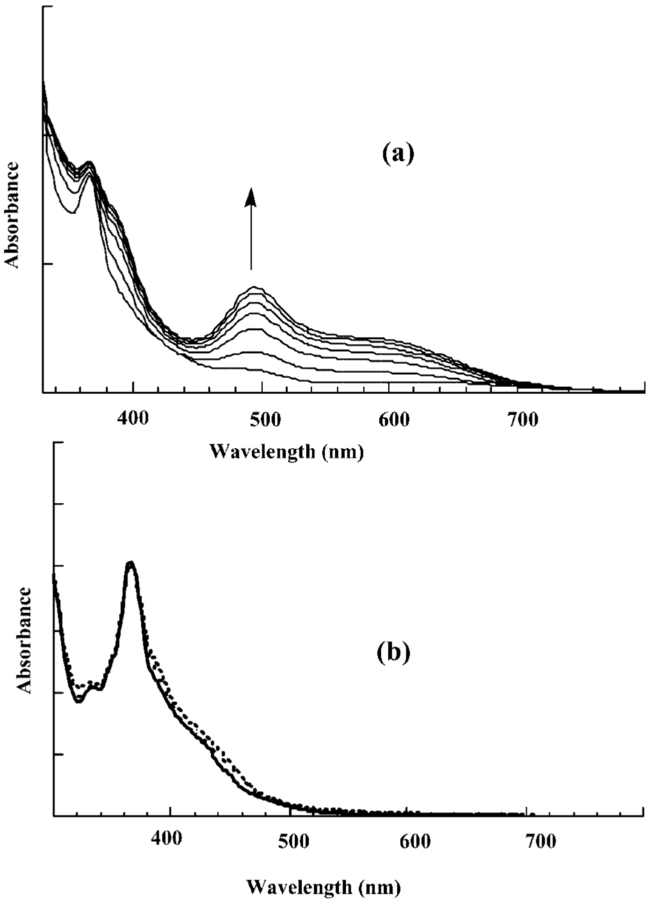


Figure 3. Spectral changes (every 5 h) of complexes **1** (a, 0.25 mM) and **2** (b, 0.25 mM) in acetonitrile (with exposure to air)

$$\begin{aligned}&[\mathrm{MoO(Bubpy)(mnt)}] + \mathrm{O_2} \rightarrow [\mathrm{MoO_2(Bubpy)(mnt)}],\\ &\quad [\mathrm{MoO(Bubpy)(mnt)}] + [\mathrm{MoO_2(Bubpy)(mnt)}] \rightarrow\\ &\qquad [\mathrm{Mo_2O_3(Bu_2bpy)_2(mnt)_2}]\end{aligned} \tag{1}$$

In contrast, complex **2** did not react with molecular oxygen in CH_3CN (Figure 3, b). Although the redox potentials assigned to $Mo^{IV/V}$ for **1** and **2** were almost the same, 0.20 and 0.22 V vs. Ag/Ag^+, respectively, both complexes showed largely different reactivities toward molecular oxygen. The rigid molybdenum(IV)-porphyrin complex [Mo^{IV}O(oep)] (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato) forms the dimerized [$\{Mo^{V}O(oep)\}_2(\mu\text{-}O)$] via intermediate [$Mo^{VI}O(O_2)$(oep)] upon treatment with O_2.[10] ^1H NMR studies indicate that complex **2** has a flexible ethylenediamine ligand, although complex **1** has a rigid bipyridyl ligand. Therefore, for the dimerization, an outer-sphere oxidation process is excluded but an inner-sphere oxidation process by O_2 may occur. Both the steric bulkiness of the four ethyl groups in **2**, and its dynamic behavior, prevent interaction of the molybdenum center in **2** with O_2 and so its reactivity differs from that of **1**. Xanthin oxidase, which has one dithiolane, prevents dimerization and retains a mononuclear molybdenum structure when exposed to molecular oxygen.[11] Thus, judging from the above described results, **2** rather than **1** may serve as an effective xanthine oxidase model. We have further demonstrated that the reactivity of the molybdenum-mono-dithiolene complexes, [MoO(mnt)], could be changed by varying the ancillary ligands.

Some of molybdenum(IV) mono-oxo bis(dithiolene) complexes react with trimethylamine N-oxide (Me_3NO) to give the corresponding molybdenum(VI) di-oxo complexes of [MoO_2(dithiolene)$_2$]$^{2-}$.[3f] When complexes **1** and **2** were treated with Me_3NO, electronic spectral changes were observed, but the corresponding molybdenum(VI) di-oxo complexes could not be isolated and their reaction could not be followed precisely (Figure 4).

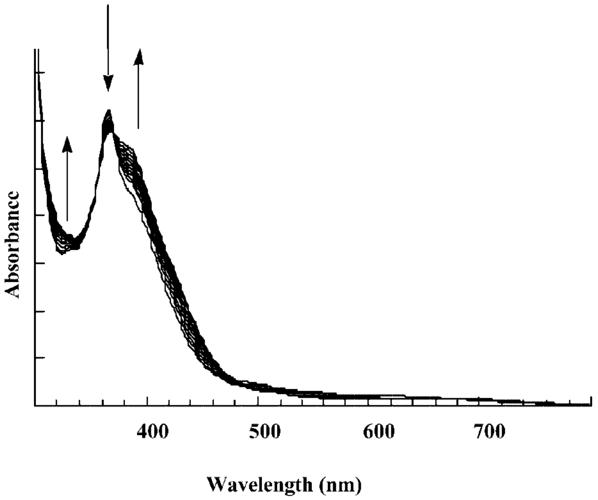


Figure 4. Spectral change (every 1 h) of the complex formed (0.25 mM) after addition of $(CH_3)_3NO$ (5.0 mM) in CH_3CN to **1**

Crystal Structure of [$Mo_2O_3(Bu_2bpy)_2(mnt)_2$]

The molecular structure of complex **3** is shown in Figure 5 and the selected bond lengths [Å] and angles [°] are summarized in Table 1.

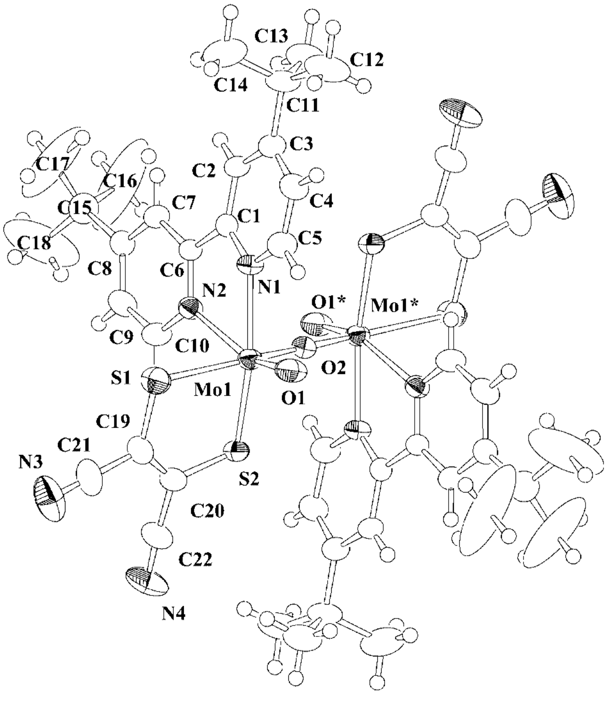


Figure 5. Molecular structure of complex [$Mo_2O_3(Bu_2bpy)_2(mnt)_2$] (**3**) with the atomic numbering scheme showing 50% probability thermal ellipsoids

Table 1. Selected bond lengths [Å] and angles [°] for **3**·$2CH_3C(O)CH_3$

Mo1−S1	2.464(1)	Mo1−S2	2.394(1)
Mo1−O1	1.680(4)	Mo1−O2	1.8694(4)
Mo1−N1	2.238(4)	Mo1−N2	2.327(4)
S1−C19	1.738(6)	S2−C20	1.735(6)
C19−C20	1.359(8)		
S1−Mo1−S2	84.38(5)	S1−Mo1−O1	96.7(2)
S1−Mo1−O2	158.60(4)	S1−Mo1−N1	95.7(1)
S1−Mo1−N2	81.7(1)	S2−Mo1−O1	107.7(1)
S2−Mo1−O2	83.60(3)	S2−Mo1−N1	164.3(1)
S2−Mo1−N2	95.0(1)	O1−Mo1−O2	103.8(1)
O1−Mo1−N1	88.0(2)	O1−Mo1−N2	157.0(2)
O2−Mo1−N1	91.2(1)	O2−Mo1−N2	81.81(10)
N1−Mo1−N2	69.5(1)	Mo1−S1−C19	103.1(2)
Mo1−S2−C20	105.7(2)		

Complex **3** has a [Mo_2O_3] neutral core, with each molybdenum center in a distorted octahedral geometry provided by two nitrogens of one Bu_2bpy, two sulfurs of one mnt, a terminal oxo group, and the bridging oxo group which occupies a crystallographic inversion center. Its [Mo_2O_3] core is strictly *anti* planar, in which one molybdenum has an O2N2S2 donor set. The S1 atom is *trans* to the bridging oxygen O2; S2 is *trans* to N1; and N2 is *trans* to a terminal oxygen O1. Similar structures have been reported for [$Mo_2O_3(2\text{-}SC_5H_3N)_4$],[12] [$Mo_2O_3(2\text{-}SC_5H_3N\text{-}3\text{-}SiNe_3)_4$] (2-$SC_5H_3N_4$ = pyridine-2-thiolato),[13] [Mo_2O_3(*N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptophenyl)ethylenediamine$)_2$],[14] and [Mo_2O_3(*N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)ethylenediamine$)_2$].[15] In these complexes, all nitrogen donors occupied *trans* positions to the oxygen donors, while the sulfur donors were *cis* to each other. In complex **3**, a somewhat longer Mo1−N2 bond length [2.327(4) Å] than that of Mo1−N1 [2.238(4) Å] was observed due to the *trans* influence of a strong Mo-dπ and terminal O−pπ interaction. A similar trend is found for Mo−S1 [2.464(1) Å] and Mo-S2 [2.394(1) Å] bond lengths. The $Mo-O_{terminal}$ [1.680(4) Å] and $Mo-O_{bridging}$ [1.8694(4) Å] distances are in the range found in the above example [Mo_2O_3] complexes. Although some dinuclear molybdenum(V) complexes with one dithiolene per molybdenum center have been reported by Holm et al., their dimers have a di-oxo bridged Mo_2O_4 core of [$Mo_2O_2(\mu\text{-}O)_2(bdt)_2$]$^{2-}$.[7] Moreover, mono-dithiolene molybdenum(VI) ($Et_4N)_2\{Mo^{VI}O_2(Ph_3Si\text{-}bdt)\}_2(\mu\text{-}O)$], having a dinuclear core bridged by one oxo group, has also been reported.[16] Since complex **3** has a mono-oxo bridged dimolybdenum(V) core, it is a new kind of mono-dithiolene dimolybdenum complex.

Experimental Section

Materials: The ligands Bu_2bpy and Na_2mnt were prepared as described in the literature.[17,18] Acetonitrile was dried with calcium hydride and distilled under dinitrogen. Methanol was dried over molecular sieves and also distilled under dinitrogen. THF was distilled from sodium/benzophenone. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized twice from hot ethanol. All other commercially available reagents were used as purchased. The preparation of complexes **1**−**3** was carried out under dinitrogen or argon.

Preparation of Complexes

[MoO(mnt)(Bu_2bpy)] (1): Na_2mnt (47 mg, 0.26 mmol) was added to a methanolic solution (10 mL) of [$MoO_2Cl_2(Bu_2bpy)$] (**4**, see below) (60 mg, 0.13 mmol) and the solution was stirred for 1 day. After concentration of the solution to 3 mL, a yellow−brown microcrystalline powder, deposited upon addition of H_2O (1 mL), was collected by filtration and dried in vacuo. Yield 38 mg (56%). $C_{22}H_{24}MoN_4OS_2$ (520.53): calcd. C 50.76, H 4.65, N 10.76; found C 51.05, H 4.73, N 10.58. ESI-MS (acetonitrile): *m*/*z* = 561 [M + K]$^+$. IR (KBr): $\tilde{\nu}$ = 2195 [ν(C−N)], 939 cm^{-1} [ν(Mo=O)]. UV/Vis (acetonitrile): λ (ε, mol dm^3 cm^{-1}) = 607 (110), 492 (261), 369 (4090), 335 nm (2466). ^{1}H NMR ([D_3]acetonitrile, 25 °C): δ = 8.61 (d, 2 H), 8.44 (s, 2 H), 7.68 (d, 2 H), and 1.42 (s, 18 H) ppm. Redox potential (acetonitrile): $Mo^{V/IV}$, 0.20 V (reversible) vs. Ag/Ag$^+$.

[MoO(mnt)(Et_4en)] (2): MoO_2Cl_2 (99 mg, 0.5 mmol) was added to CH_3OH (10 mL) and then *N*,*N*′-tetraethylethylenediamine (102 μL, 0.5 mmol) was injected. After 15 min stirring, Na_2mnt (93 mg, 0.5 mmol) was gradually added to the solution. A yellow−orange microcrystalline powder then precipitated from the resulting red−brown solution, and was collected by filtration and dried in vacuo. Yield 81 mg (38%). $C_{14}H_{24}MoN_4OS_2$ (424.04): calcd. C 39.62, H 5.70, N 13.20; found C 39.91, H 5.56, N 12.98. ESI-MS (acetonitrile): *m*/*z* = 465 [M + K]$^+$. IR (KBr): $\tilde{\nu}$ = 2194 [ν(C−N)], 906 cm^{-1} [ν(Mo=O)]. UV/Vis (acetonitrile): λ (ε, mol dm^3 cm^{-1}) = 512 (512), 365 (7771), 331 nm (4167). ^{1}H NMR ([D_3]acetonitrile, 25 °C.): δ = 3.05 (br., 4 H), 3.00 (d, 8 H), and 1.22 (t, 12 H) ppm. Redox potential (acetonitrile): $Mo^{V/IV}$, 0.20 V (reversible) vs. Ag/Ag^+.

$[Mo_2O_3(mnt)_2(Bu_2bpy)_2]$ (3). Method a: Na_2mnt (93 mg, 0.5 mmol) was added to a colorless acetone solution (10 mL) containing MoO_2Cl_2 (99 mg, 0.5 mmol) and Bu_2bpy (134 mg, 0.5 mmol). The resulting orange suspension was then stirred until a clear orange solution was obtained, which on exposure to air for 1 day gave black crystals of **3**. The crystals were collected by filtration and dried in air. Yield 115 mg (44%, based on two molybdenums).

Method b: Complex **1** (30 mg, 0.058 mmol) was dissolved in CH_3CN (10 mL) under argon to give a solution that upon exposure to air changed from yellow to blue-gray. Overnight, black−purple crystals then precipitated out of the solution, and were collected by filtration and dried in air. Yield 24 mg (78%). Precipitates obtained by methods a and b have the same IR and UV/Vis spectra.

$C_{44}H_{48}Mo_2N_8O_3S_4$ (1057.04): calcd. C 49.99, H 4.58, N 10.60; found C 50.21, H 4.54, N 10.55. ESI-MS (dimethylformamide): $m/z = 1060$ $[M]^-$. IR (KBr): $\tilde{\nu} = 2205$ [ν(C−N)], 947 cm^{-1} [ν(Mo=O)]. Redox potential (dimethylformamide): $Mo^VMo^V/Mo^{IV}Mo^V$, −0.93 V (reversible) and −1.64 V (E_{pc}, irreversible) vs. Ag/Ag^+. UV/Vis (acetonitrile): λ (ε, mol dm^3 cm^{-1}) = 604 (sh) (663), 498 (1390), 342 nm (1060).

$[MoO_2Cl_2(Bu_2bpy)]$ (4): Bu_2bpy (134 mg, 0.5 mmol) was added to a freshly distilled THF solution (10 mL) containing MoO_2Cl_2 (99 mg, 0.5 mmol). The resulting colorless solution was evaporated to 2 mL to give a white microcrystalline powder, which was collected by filtration and dried in air. Yield 203 mg (87%). IR (KBr): $\tilde{\nu} = 939$, 908 cm^{-1} [ν(Mo=O)]. ^1H NMR ([D_3]acetonitrile, 25 °C): δ = 9.46 (d, 2 H), 9.00 (s, 2 H), 8.07 (d, 2 H), 1.50 (s, 18 H) ppm.

X-ray Crystallographic Study: A single crystal of $[Mo_2O_3(Bu_2bpy)_2(mnt)_2]$ (**3**) was obtained upon standing for one day from the acetone solution, and a single crystal of $[MoO_2Cl_2(Bu_2bpy)]$ (**4**) was obtained by recrystallization from acetone solution. Each crystal was attached to the top of a glass fiber. X-ray data of complex **3** and **4** were then collected with graphitec-monochromated Mo-*K*α radiation on a Rigaku/MSC Mercury CCD diffractometer at −100 °C and on a Rigaku AFC7R diffractometer at −50 °C, respectively. The structures were solved by direct methods (SIR, 92)[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms of all complexes were refined anisotropically by the full-matrix least-squares method. All calculations were performed using TEXSAN.[21] Further crystallographic data are summarized in Table 2.

Complex **4** (see Supporting Information, Figure S2 and Table S1) has a distorted octahedral arrangement about the molybdenum atom, with two oxygen atoms in *cis* positions and the two chlorine atoms in *trans* positions. The bond lengths and angles around the molybdenum center are very similar to those of $[MoO_2Cl_2$(4,4′-dimethyl-2,2′-bipyridine)][22] and $[Mo_2O_2Cl_2$(1,10-phenanthroline)];[23] the structural arrangements are also the same in these complexes and **4**. It is noteworthy that **4** crystallized in a chiral space group $P2_12_12_1$, indicating that spontaneous resolution of complex occurred. Conversely, $[MoO_2Cl_2$(4,4′-dimethyl-2,2′-bipyridine)] crystallized in an achiral space group $P2_1/n$.

CCDC-198986 and -198987 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for $[Mo_2O_3(Bu_2bpy)_2(mnt)_2]\cdot 2CH_3C(O)CH_3$ [**3**$\cdot 2CH_3C(O)CH_3$] and $[MoO_2Cl_2(Bu_2bpy)]$ (**4**)

	3$\cdot 2CH_3C(O)CH_3$	4
Empirical formula	$C_{50}H_{60}Mo_2N_8O_5S_4$	$C_{18}H_{24}Cl_2MoN_2O_2$
Formula mass	1173.19	467.25
T [°C]	−100	−50.0
a [Å]	11.331(1)	13.451(4)
b [Å]	21.412(2)	18.221(6)
c [Å]	11.636(1)	8.405(3)
β [°]	91.392(6)	
V [$Å^3$]	2822.4(5)	2060(1)
Z	2	4
Space group	$P2_1/a$ (no. 14)	$P2_12_12_1$ (no. 19)
$d_{calcd.}$ [g/cm^3]	1.380	1.506
Crystal size [mm]	0.20 × 0.20 × 0.20	0.33 × 0.26 × 0.26
μ(Mo-*K*α) [cm^{-1}]	6.41	9.08
No. of unique reflns.	6635	2639
No. obsd. reflns.	5800, all	1905, $I > 2.0\sigma(I_o)$
R (%)	8.3[a]	4.1[b]
Rw (%)	22.2[c]	5.1[d]

[a] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $Rw = [(\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]]^{1/2}$. [d] $Rw = [(\Sigma w(F_o - F_c)^2/\Sigma w(Fo^2)^2]]^{1/2}$.

Other Measurements: Cyclic voltammetry was performed with a Hokuto HA-501 potentiostat and a Hokuto HB-105 function generator, equipped with a Graphtec WX2400 X-Y recorder, or a Hokuto HZ-3000. The working and counter electrodes were a glassy-carbon disk and a platinum wire, respectively. Cyclic voltammograms were recorded at 50 mV·s^{-1}. The sample solutions (ca. 1.0 mᴍ) in 0.1 ᴍ $TBAPF_6$/acetonitrile were deoxygenated with a stream of dinitrogen gas. The reference electrode was Ag/Ag^+ and the half-wave potential of Fc^+/Fc [$E_{1/2}(Fc^{+/0})$] vs. Ag/Ag^+ was 0.015 V in CH_3CN. Electronic spectra were recorded with a Shimazu 2550 or HP 5254A spectrophotometer at 20 °C. IR spectra were recorded with a Perkin−Elmer Spectrum GX infrared spectrophotometer. ^1H NMR spectra were measured with a JEOL-Lambda 300 (300 MHz) or Bruker AVANCE 600 (600 MHz) spectrometer. ESI-MS was obtained with a PE SCIEX API300.

Supporting Information Available (see the footnote on the first page of this article): ORTEP drawings $(mnt)_2^{2-}$, the oxidized form of mnt^{2-}, (Figure S1) and complex **4** (Figure S2). Selected bond lengths and angles of complex **4** (Table S1).

Acknowledgments

This work was partly supported by the Joint Studies Program (2001−2002) of the Institute for Molecular Science, Japan and by CREST of the Japan Science and Technology Corporation.

---

[1] [1a] R. Hille, *Chem. Rev.* **1996**, *96*, 2757. [1b] W. R. Hagen, A. F. Arendsen, *Struct. Bonding* **1998**, *90*, 161.

[2] A. Messerschmidt, R. Huber, T. Poulos, K. Wieghardt, "*Handbook of Metalloproteins*", John Wiley & Sons, New York, **2000**, *2*, 1024.

[3] [3a] B. S. Lim, R. H. Holm, *J. Am. Chem. Soc.* **2001**, *123*, 1920. [3b] B. S. Lim, J. P. Donahue, *Inorg. Chem.* **2000**, *39*, 263. [3c] J. P. Donahue, C. R. Goldsmith, U. Nadiminti, R. H. Holm, *J. Am. Chem. Soc.* **1998**, *120*, 12869. [3d] H. Oku, N. Ueyama, A.

Nakamura, *Inorg. Chem.* **1997**, *36*, 1504. [3e] N. Ueyama, H. Oku, M. Kondo, T. Okamura, N. Yoshinaga, A. Nakamura, *Inorg. Chem.* **1996**, *35*, 643. [3f] H. Oku, N. Ueyama, M. Kondo, A. Nakamura, *Inorg. Chem.* **1994**, *33*, 209.

[4] [4a] E. S. Davies, R. L. Beddoes, D. Collison, A. Dinsmore, A. Docrat, J. A. Joule, C. R. Wilson, C. D. Garner, *J. Chem. Soc., Dalton Trans.* **1997**, 3985. [4b] S. K. Das, P. K. Chaudhury, D. Biswas, S. Sarkar, *J. Am. Chem. Soc.* **1994**, *116*, 9061. [4c] D. Coucouvanis, A. Hadjikyriacou, A. Toupadakis, S-M. Koo, O. Ileperuma, M. Draganjac, A. Salifoglou, *Inorg. Chem.* **1991**, *30*, 754. [4d] K. Nagarajan, P. K. Chaudhury, B. R. Srinivasan, S. Sarkar, *Chem. Commun.* **2001**, 1786.

[5] K. M. Nicholas, M. A. Khan, *Inorg. Chem.* **1987**, *26*, 1633.

[6] I. K. Dhawan, J. H. Enemark, *Inorg. Chem.* **1996**, *35*, 4873.

[7] B. S. Lim, M. W. Willer, M. Miao, R. H. Holm, *J. Am. Chem. Soc.* **2001**, *123*, 8343.

[8] R. Hazama, K. Umakoshi, A. Ichimura, S. Ikari, Y. Sasaki, T. Ito, *Bull. Chem. Soc., Jpn.* **1995**, *68*, 456.

[9] R. H. Holm, *Coord. Chem. Rev.* **1990**, *101*, 183.

[10] J. W. Bucher, "*The Porphyrins*", (Ed.: D. Dolphin), Academic, New York, **1978**, *1*, 389.

[11] C. Enroth, B. T. Eger, K. Okamoto, T. Nishino, T. Nishino, E. F. Pai, *Proc. Natl. Acad. Sci.* **2000**, *20*, 10723.

[12] F. A. Cotton, P. E. Fanwick, J. W. Fitch, *Inorg. Chem.* **1978**, *17*, 3254.

[13] E. Block, M. Gernon, H. Kang, G. Ofori-Okai, J. Zubieta, *Inorg. Chem.* **1991**, *30*, 1736.

[14] K. R. Barnard, M. Bruck, S. Huber, C. Grittini, J. H. Enemark, R. W. Gable, A. G. Wedd, *Inorg. Chem.* **1997**, *36*, 637.

[15] P. L. Dahlstrom, J. R. Hyder, P. A. Vella, J. Zubieta, *Inorg. Chem.* **1982**, *21*, 927.

[16] H. Oku, N. Ueyama, A. Nakamura, *Bull. Chem. Soc., Jpn.* **1999**, *72*, 2261.

[17] T. B. Hadda, H. L. Bozec, *Inorg. Chim. Acta* **1993**, *204*, 103.

[18] A. Davison, R. H. Holm, *Inorg. Synth.* **1967**, *10*, 8.

[19] A. Altomare, M. C. Burla, M. Camalli, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[20] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosmanm, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, The DIRDIF Program System. Technical Report: Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.

[21] TEXSAN. Single Crystal Structure Analysis Pakage. Molecular Structure Corporation: The Woodlands, TX 77382, **1992**, USA.

[22] D. M. Baird, F. L. Yang, D. J. Kavanaugh, G. Finness, K. R. Dunber, *Polyhedron* **1996**, *15*, 2597.

[23] P. B. Viossat, N. Rodier, *Acta Crystallogr., Sect. B* **1979**, *35*, 2715.

Received November 22, 2002