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Synthesis, Structure and Proton-Coupled Electron Transfer of μ-Oxo-μ-chloro and μ-Oxo-μ-alkoxo Dimeric Molybdenum(III) Ethylenediamine Complexes

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An oxo- and chloro-bridged dinuclear molybdenum(III) ethylenediamine complex, $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$, was synthesized by the reaction of $[MoCl_3(thf)_3]$ with ethylenediamine in DMF. μ-Oxo-μ-alkoxo-bridged dimolybdenum(III) ethylenediamine complexes $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$, $[Mo_2(\mu\text{-O})(\mu\text{-OEt})(en)_4]^{3+}$, and $[Mo_2(\mu\text{-O})(\mu\text{-OPr})(en)_4]^{3+}$ were obtained by reactions of the mononuclear complex with ethylenediamine in methanol, ethanol, and propanol, respectively, where each solution contained LiBr. Bridged dimeric structures of these complexes were determined by X-ray crystallography. In an acidic aqueous solution, these oxo-bridged complexes underwent protonation on the bridging oxygen atoms and changes to the corresponding hydroxo-bridged complexes. Cyclic voltammetric measurements (pH 1.0–10.0) of complexes $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$, $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$, and $[Mo_2(\mu\text{-O})(\mu\text{-OEt})(en)_4]^{3+}$ clearly showed that, accompanied by the oxidation of the complex, the coordinated amine is deprotonated, and the complex becomes a corresponding amido-coordinated complex.

In the periodic table, although molybdenum belongs to the same family as chromium, the similarity between both elements is rather limited. Whereas Cr(III) complexes with a variety of ligands exist in stable states, Mo(III) complexes with only limited kinds of ligands are known to be stable, and most of them are readily oxidized in air. Consequently, it appears to be valuable to study the coordination chemistry of Mo(III).

The only molybdenum(III) amine and other N donor heterocyclic ligand complexes that have been reported and well characterized are: $[Mo(tacn)X_3]$ (tacn; 1,4,7-triazacyclononane, X = Cl^-, Br^-, I^-, NCS^-),[1] $[Mo_2(\mu\text{-OH})_2X_2(tacn)_2]^{n+}$ (X = Cl^-, Br^-, OH^-, H_2O; n, dependent on X),[2–4] $[Mo_2(\mu\text{-OH})_2X(tacn)_2]^{n+}$ (X = HCO_2^-, $CH_3CO_2^-$, CO_3^{2-}; n, dependent on X),[2,4,5] $[Mo_2(\mu\text{-OH})(\mu\text{-Br})Br_2(tacn)_2]^{2-}$,[3] $[MoLX_2]$ (L = cyclam; 1,4,8,11-tetraazacyclotetradecane, cyca; *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, [15]aneN_4; 1,4,8,12-tetraazacyclopentadecane, X = Cl^-, $CF_3SO_3^-$),[6,7] $[Mo(NH_3)_3X_3]$ (X = Cl^-, $CF_3SO_3^-$),[8] $[Mo_2(\mu\text{-O})_2(H_2O)_2(edta)]^{2-}$ (edta; ethylenediaminetetraacetic acid),[9] $[Mo_2(\mu\text{-OH})_2X_2(edta)]^{n-}$ (X = H_2O, NCS^-; n, dependent on X),[10] $[Mo_2(\mu\text{-OH})_2X(edta)]^-$ (X = $CH_3CO_2^-$, HCO_2^-),[10] $[MoX_3(py)_3]$ (py; pyridine, X = Cl, Br),[11] $[Mo(bpy)_2Cl_2]^+$ (bpy; 2,2′-bipyridine), and $[Mo(phen)_2Cl_2]^+$ (phen; 1,10-phenanthroline).[12]

This paper describes the syntheses of new oxo- and chloro-bridged or oxo- and alkoxo-bridged dinuclear molybdenum(III) ethylenediamine complexes, $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$ and $[Mo_2(\mu\text{-O})(\mu\text{-OR})(en)_4]^{3+}$ (R = Me, Et, Pr^n).

Various molybdenum(III) complexes with terminal and/or bridged alkoxo molybdenum(III) complexes have been reported,[13] but the present oxo- and chloro-bridged or alkoxo-bridged dinuclear molybdenum(III) complexes are previously unknown types of complexes. Furthermore, it has been found that, in the process of obtaining a molybdenum(III) amine complex, the reaction of $[MoCl_3(thf)_3]$ (thf; tetrahydrofuran) with ethylenediamine in alcohol is enhanced by the addition of LiBr.

Oxo- or hydroxo-bridged dinuclear complexes of iron or manganese have been intensively studied in close connection with the chemistry of the active sites of many metal proteins that undergo proton-coupled electron-transfer related to protonation to the bridging oxygen.[14] Exhaustive studies of the structure or electronic spectra have been made in relation to the molybdenum complexes, but no proof of the transfer has been obtained. It has now became clear that proton dissociation from coordinated amines occurs in oxo- and chloro-bridged or oxo- and alkoxo-bridged dinuclear molybdenum(III) ethylenediamine complexes. This issue is also discussed in the present paper. Preliminary reports of a part of this work have been published elsewhere.[15,16]

Experimental

All procedures were carried out under a dinitrogen or argon atmosphere.

Materials. The mononuclear complex $[MoCl_3(thf)_3]$ was synthesized according to a method described in the literature.[17]

Syntheses of Complexes. The solvents were freed from oxygen and dried.

$[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (1): Ethylenediamine (5.0 cm^3, 74.4 mmol) was added to a conical flask cooled in an ice-bath containing $[MoCl_3(thf)_3]$ (5.19 g, 12.4 mmol) dissolved in DMF (62 cm^3). Then, the solution was stirred at room temperature. After several minutes, the color of the solution turned from brick-red to dark green with the formation of a fine moss-green precipitate. The mixture was heated at ca. 80 °C for 2 h with stirring, cooled, and then filtered. The moss-green precipitate was washed with ethanol twice, giving a yield of 3.89 g. This powder was dissolved in an aqueous $Na_2S_2O_6$ solution (0.80 M, 37 cm^3; 1 M = 1 mol dm^{-3}) and filtered. The filtrate was stored in a refrigerator for 3 days to give green crystals of **1**: yield 1.45 g (32% based on $[MoCl_3(thf)_3]$). Found: C, 12.96; H, 5.31; N, 15.10; Cl, 9.5; S, 8.7%. Calcd for $C_8H_{38}N_8O_{10}Mo_2Cl_2S_2$: C, 13.10; H, 5.22; N, 15.28; Cl, 9.67; S, 8.74%.

$[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (2): Anhydrous ethylenediamine (2.80 cm^3, 41.9 mmol) was added to $[MoCl_3(thf)_3]$ (2.92 g, 7.0 mmol) in a 1.0 M $LiBr\cdot H_2O$ methanol solution (25 cm^3). Then, the mixture was heated at ca. 50 °C for 3 h, cooled to room temperature, and stored in a freezer overnight. A deposited green precipitate was filtered and washed with ethanol, giving a yield of 1.41 g. For recrystallization, this powder was dissolved in water (8.7 cm^3) and filtered. When ethanol (1.3 cm^3) was added and cooled in a refrigerator, green crystals of $[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ were obtained. Yield 0.26 g (10% based on $[MoCl_3(thf)_3]$) Found: C, 14.19; H, 5.34; N, 14.79; Br, 24.3; Cl, 4.0%. Calcd for $C_9H_{41}N_8O_5Mo_2Br_{2.2}Cl_{0.8}$: C, 14.66; H, 5.60; N, 15.19; Br, 23.84; Cl, 3.95%.

$[Mo_2(\mu\text{-}O)(\mu\text{-}OEt)_{0.8}(\mu\text{-}Cl)_{0.2}(en)_4]Br_3\cdot 3H_2O$ (3): Anhydrous ethylenediamine (1.3 cm^3, 19.92 mmol) was added to $[MoCl_3(thf)_3]$ (1.39 g, 3.32 mmol) in a 2.0 M $LiBr\cdot H_2O$–ethanol solution (33 cm^3). The mixture was then heated at ca. 60 °C for 3 h, cooled to room temperature, and stored in a refrigerator overnight. A deposited green precipitate was filtered and washed with ethanol, giving a yield of 0.31 g.

This powder was dissolved in a NaBr aqueous solution (1.0 M, 3.69 cm^3) and filtered. After the filtrate was stored in a refrigerator for 3 days, green crystals of $[Mo_2(\mu\text{-}O)(\mu\text{-}OEt)_{0.8}(\mu\text{-}Cl)_{0.2}(en)_4]Br_3\cdot 3H_2O$ were obtained. Yield 0.059 g (4% based on $[MoCl_3(thf)_3]$) Found: C, 14.76; H, 5.30; N, 14.46; Br, 30.83; Cl, 0.88%. Calcd for $C_{9.6}H_{42}N_8O_{4.8}Mo_2Br_3Cl_{0.2}$: C, 14.92; H, 5.63; N, 14.92; Br, 30.53; Cl, 0.90%.

$[Mo_2(\mu\text{-}O)(\mu\text{-}OPr^n)(en)_4]Br_3\cdot 3H_2O$ (4): Anhydrous ethylenediamine (2.46 cm^3, 36.69 mmol) was added to $[MoCl_3(thf)_3]$ (2.56 g, 6.12 mmol) in a 1.0 M $LiBr\cdot H_2O$–1-propanol solution (21 cm^3). Then, the mixture was heated at ca. 60 °C for 2 h, cooled to room temperature, and stored in a refrigerator overnight. A deposited green precipitate was filtered and washed with ethanol.

For recrystallization, this powder was dissolved in water (5.88 cm^3) and filtered. When propanol (0.93 cm^3) was added and the mixture was cooled in a refrigerator, green crystals $[Mo_2(\mu\text{-}O)(\mu\text{-}OPr^n)(en)_4]Br_3\cdot 3H_2O$ were formed. Yield 0.093 g (4% based on $[MoCl_3(thf)_3]$). Found: C, 16.65; H, 5.72; N, 14.07%. Calcd for $C_{11}H_{45}N_8O_5Mo_2Br_3$: C, 16.49; H, 5.66; N, 13.99%.

X-ray Crystal Structure Analysis of $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (1), $[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (2), and $[Mo_2(\mu\text{-}O)(\mu\text{-}OEt)_{0.8}(\mu\text{-}Cl)_{0.2}(en)_4]Br_3\cdot 3H_2O$ (3). Each of the green crystals of **1**, **2**, and **3** was sealed in a glass capillary after being coated with a small amount of silicon grease under a dinitrogen atmosphere. The crystallographic data are summarized in Table 1.

The structures of **1**, **2**, and **3** were solved by SIR-92 (direct method)[18] and expanded using Fourier techniques.[19] Non-hydrogen atoms were refined anisotropically by a full-matrix least squares method. Hydrogen atoms were included, but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[20] The values for Δf and $\Delta f'$ were those of Creagh

Table 1. Summary of Crystal Data for $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**), $[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (**2**) and $[Mo_2(\mu\text{-}O)(\mu\text{-}OEt)_{0.8}(\mu\text{-}Cl)_{0.2}(en)_4]Br_3\cdot 3H_2O$ (**3**)

Compound	**1**	**2**	**3**
Formula	$Mo_2Cl_2S_2O_{10}N_8C_8H_{38}$	$Mo_2Br_{2.2}O_5N_8C_9H_{41}Cl_{0.8}$	$Mo_2C_{9.6}N_8O_{4.8}Br_3H_{42}Cl_{0.2}$
Formula weight	733.34	737.51	785.17
Crystal color	Green, plate	Green, plate	Green, plate
Crystal size/mm^3	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.05	0.20 × 0.10 × 0.05
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pca2_1$	Cc	$P2_1/c$
a/Å	18.760(5)	17.591(2)	10.098(2)
b/Å	13.537(4)	15.294(2)	14.962(3)
c/Å	10.070(4)	10.120(3)	18.085(3)
β/°	—	111.023(9)	100.98(2)
V/Å^3	2557(1)	2541.4(8)	2682.3(9)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.905	1.927	1.944
D_{obs}/g cm^{-3}	1.89	1.96	1.94
μ(Mo-Kα)/cm^{-1}	14.08	45.72	54.68
F (000)	1488.00	1462.40	1545.60
Radiation λ/Å	Mo Kα, 0.71069[a)]	Mo Kα, 0.71070[a)]	Mo Kα, 0.71070[a)]
R[b)]	0.047	0.068	0.036
R_W[c)]	0.068	0.105	0.056

a) Graphite monochromated. b) $R = \Sigma \| F_O| - |F_C\| / \Sigma |F_O|$. c) $R_W = [\Sigma w(|F_O| - |F_C|)^2 / \Sigma w F_O{}^2]^{1/2}$; $w = 1/\sigma^2(F_O) = [\sigma_C{}^2(F_O) + p^2/4(F_O)^2]^{-1}$.

and McAuley.[21] The values for the mass-attenuation coefficients were those of Creagh and Hubbel.[22] All calculations were performed using the TEXSAN crystallography software package[23] (Molecular Structure Corporation).

The X-ray analysis of **1** was straightforward, but that of **2** was a little difficult; an elemental analysis of **2** revealed the presence of chloride and bromide anions. Each of the occupancy factors of the three bromide anions was set to 0.73 (= 2.2/3), and that of chloride 0.27 (= 0.8/3); the positions of the chloride anions were constrained to take the same position as the bromide anions. As for **3**, a disorder of the bridging moiety was observed, that is, the presence of an additional bridge μ-Cl was disclosed by Fourier techniques. The occupancy factors for μ-OEt and μ-Cl were determined so as to fit the elemental analyses of the bromide and chloride, which gave reasonable temperature factors for both of the bridging groups. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 207710–207712.

Instruments. UV-visible spectra were recorded on JASCO U-best V-550 and Shimadzu UV-2100 spectrophotometers. A Perkin-Elmer 2400 II CHN analyzer was used to analyze the carbon, hydrogen, and nitrogen. Cyclic voltammetry measurements were performed with an ALS-609A electrochemical analyzer using a glassy carbon disk electrode (3 mm diameter), an Ag/AgCl, and a platinum wire as the working, reference, and counter electrodes, respectively. The surface of the glassy carbon electrode was polished with a 0.3 µm alumina slurry before each voltammetric run. The pH of the electrolytic solution was controlled using a buffer solution. The composition and pH range of the buffer solution used were 0.05 M KCl–HCl (pH 1.0–2.0) and 0.1 M NaH_2PO_4–NaOH (pH 2.5–10.0), respectively. The buffer solutions were prepared by dissolving reagent-grade chemicals in water purified with a MillQ-Lab. Samples were dissolved in the above mentioned buffer solution so as to make ca. 0.5 mmol solutions. To measure the electronic spectra, the pH of the solution was measured on a Toko CE103CS composite-type glass electrode and a Toko TP-1000 digital pH meter or a Horiba 6069-10C composite-type glass electrode and a Horiba F-23 pH meter.

Results and Discussion

Syntheses. The mononuclear complex $[MoCl_3(thf)_3]$ reacts with ethylenediamine in DMF to give the oxo- and chloro-bridged dimeric molybdenum(III) ethylenediamine complex $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$, whereas the reaction rate in alcohols is very slow, and a considerable amount of $[MoCl_3(thf)_3]$ remains unchanged. The reaction rates in alcohols are remarkably increased by the addition of LiBr (1 or 2 M); the reaction proceeds even at room temperature, and is completed by heating at 50–60 °C and stirring; in this way, oxo- and alkoxo-bridged dimeric molybdenum(III) ethylenediamine complexes, $[Mo_2(\mu\text{-O})(\mu\text{-OR})(en)_4]^{3+}$ (R = Me, Et, *n*-Pr), are formed. The addition of LiCl also enhanced the reaction, though it was not as much as LiBr, whereas the addition of NaOEt did not enhanced it. Therefore, although an enhancement by lithium ion seems to be operative, the mechanism is not clear at present. Although enhancements by the addition of lithium salts are known for some organic reactions,[24] no such an enhancement by Li salts, to our knowledge, has been reported in inorganic reactions. Of the three μ-oxo-μ-alkoxo complexes, μ-oxo-μ-OMe and μ-oxo-μ-OPr^n complexes were isolated as pure samples by recrystallization, while pure μ-oxo-μ-OEt complex was not isolated by recrystallization; although attempts were made to obtain pure samples of the μ-oxo-μ-OEt complex, all of the products were found to be 8:2 mixtures of μ-oxo-μ-OEt and μ-oxo-μ-Cl complexes, by means of elemental analysis and X-ray crystallography.

Hyldtoft et al. and Jacobsen et al. prepared several mononuclear molybdenum(III) amine complexes $[Mo(cyclam)Cl_2]^+$,[6] $[Mo(cyca)Cl_2]^+$,[6] $[Mo([15]aneN_4)Cl_2]^+$,[7] and $[Mo(NH_3)_3Cl_3]$[8] through the reaction of $[MoCl_3(thf)_3]$ with macrocyclic polyamines or NH_3 in THF; on the other hand, we prepared dinuclear molybdenum(III) amine complexes through the reaction of the same starting material $[MoCl_3(thf)_3]$ with noncyclic ethylenediamine in DMF or alcohol.

By recrystallization, green crystals $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**), $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (**2**), $[Mo_2(\mu\text{-O})(\mu\text{-OEt})_{0.8}(\mu\text{-Cl})_{0.2}(en)_4]Br_3\cdot 3H_2O$ (**3**), and $[Mo_2(\mu\text{-O})(\mu\text{-O-}n\text{-Pr})(en)_4]Br_3\cdot 3H_2O$ (**4**) were obtained, and the X-ray crystal structures of **1**, **2**, **3**, were determined from among these. The crystals of complex **2** were obtained even when ethanol was not added or when methanol was added instead of ethanol upon recrystallization, though the size of the crystals was smaller, and the quantity was reduced. There has been no reported example of the formation of μ-oxo-μ-chloro or μ-oxo-μ-alkoxo dimeric molybdenum(III) complexes. These molybdenum(III) complexes are very sensitive to air both in solids and in aqueous solutions. These complexes hardly dissolve in organic solvents, such as DMF, THF, MeOH, and EtOH.

X-ray Crystal Structure of $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4](S_2O_6)Cl\cdot 3H_2O$ (1), $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (2), and $[Mo_2(\mu\text{-O})(\mu\text{-OEt})_{0.8}(\mu\text{-Cl})_{0.2}(en)_4]Br_3\cdot H_2O$ (3). An X-ray analysis of **1** and **2** has revealed the existence of μ-oxo-μ-chloro and μ-oxo-μ-methoxo dinuclear molybdenum cores, respectively, and has proved the coordination of two ethylenediamine molecules to each of the molybdenum atoms (Figs. 1 and 2). An X-ray analysis has also clarified that the cation of **3** consists of $[Mo_2(\mu\text{-O})(\mu\text{-OEt})(en)_4]^{3+}$ and $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$ in the ratio of 8 to 2. A perspective view of the cation of **3** is shown in Fig. 3, where the minor component of μ-Cl is not included

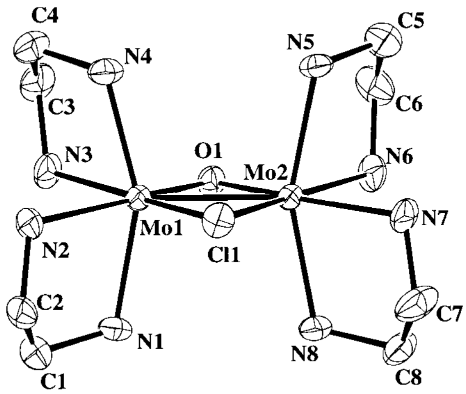


Fig. 1. Perspective view of the cation in $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**).

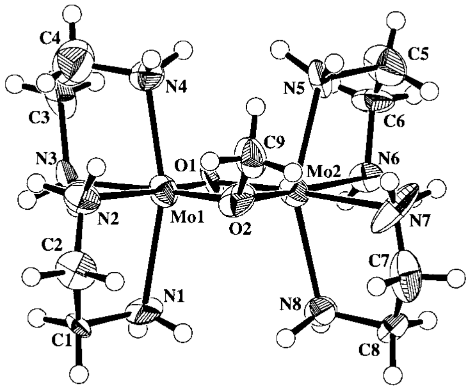


Fig. 2. Perspective view of the cation in $[\mathrm{Mo_2}(\mu\text{-O})(\mu\text{-OMe})(\mathrm{en})_4]\mathrm{Br_{2.2}Cl_{0.8}}\cdot 3\mathrm{H_2O}$ (**2**).

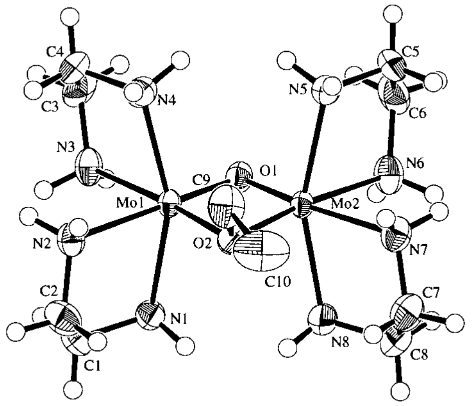


Fig. 3. Perspective view of the except minor $\mathrm{Cl^-}$ ion from the cation in $[\mathrm{Mo_2}(\mu\text{-O})(\mu\text{-OEt})_{0.8}(\mu\text{-Cl})_{0.2}(\mathrm{en})_4]\mathrm{Br_3}\cdot 3\mathrm{H_2O}$ (**3**).

Table 2. Selected Bond Distances (Å) and Angles (°) for $[\mathrm{Mo_2}(\mu\text{-O})(\mu\text{-Cl})(\mathrm{en})_4](\mathrm{S_2O_6})\mathrm{Cl}\cdot 3\mathrm{H_2O}$ (**1**)

Bond distances		Bond distances	
Mo1–Mo2	2.495(1)		
Mo1–O1	1.928(6)	Mo1–Cl1	2.428(2)
Mo2–O1	1.921(6)	Mo2–Cl1	2.436(2)
Mo1–N1	2.234(7)	Mo2–N5	2.230(7)
Mo1–N2	2.276(7)	Mo2–N6	2.216(8)
Mo1–N3	2.236(7)	Mo2–N7	2.277(7)
Mo1–N4	2.205(7)	Mo2–N8	2.231(7)
N1–C1	1.47(1)	N5–C5	1.49(1)
N2–C2	1.49(1)	N6–C6	1.47(1)
N3–C3	1.48(1)	N7–C7	1.50(1)
N4–C4	1.50(1)	N8–C8	1.51(1)
C1–C2	1.50(2)	C5–C6	1.52(2)
C3–C4	1.49(2)	C7–C8	1.47(2)
Bond angles		Bond angles	
Mo2–Mo1–Cl1	59.30(6)	Mo2–Mo1–O1	49.5(2)
Mo1–Mo2–Cl1	58.98(6)	Mo1–Mo2–O1	49.7(2)
Cl1–Mo1–O1	108.7(2)	Mo1–Cl1–Mo2	61.73(6)
Cl1–Mo2–O1	108.7(2)	Mo1–O1–Mo2	80.8(2)
Mo2–Mo1–N1	99.8(2)	Mo1–Mo2–N5	101.2(2)
Mo2–Mo1–N4	104.1(2)	Mo1–Mo2–N8	100.6(2)
N1–Mo1–N4	156.0(3)	N5–Mo2–N8	158.2(3)

Table 3. Selected Bond Distances (Å) and Angles (°) for $[\mathrm{Mo_2}(\mu\text{-O})(\mu\text{-OMe})(\mathrm{en})_4]\mathrm{Br_{2.2}Cl_{0.8}}\cdot 3\mathrm{H_2O}$ (**2**)

Bond distances		Bond distances	
Mo1–Mo2	2.442(1)	O2–C9	1.48(2)
Mo1–O1	2.13(1)	Mo1–O2	1.93(1)
Mo2–O1	2.15(1)	Mo2–O2	1.91(2)
Mo1–N1	2.21(1)	Mo2–N5	2.24(2)
Mo1–N2	2.26(2)	Mo2–N6	2.24(1)
Mo1–N3	2.35(2)	Mo2–N7	2.19(2)
Mo1–N4	2.21(1)	Mo2–N8	2.28(2)
N1–C1	1.35(4)	N5–C5	1.67(2)
N2–C2	1.51(5)	N6–C6	1.50(2)
N3–C3	1.55(3)	N7–C7	1.46(2)
N4–C4	1.54(3)	N8–C8	1.40(2)
C1–C2	1.54(4)	C5–C6	1.42(3)
C3–C4	1.51(3)	C7–C8	1.51(2)
Bond angles		Bond angles	
Mo2–Mo1–O1	55.7(3)	Mo2–Mo1–O2	50.0(5)
Mo1–Mo2–O1	54.7(3)	Mo1–Mo2–O2	50.8(4)
O1–Mo1–O2	105.6(6)	Mo1–O1–Mo2	69.7(4)
O1–Mo2–O2	105.4(6)	Mo1–O2–Mo2	79.2(5)
Mo1–O2–C9	131(1)	Mo2–O2–C9	132(1)
Mo2–Mo1–N1	103.4(4)	Mo1–Mo2–N5	98.8(4)
Mo2–Mo1–N4	100.0(4)	Mo1–Mo2–N8	101.7(4)
N1–Mo1–N4	156.4(5)	N5–Mo2–N8	158.0(6)

Table 4. Selected Bond Distances (Å) and Angles (°) for $[\mathrm{Mo_2}(\mu\text{-O})(\mu\text{-OEt})_{0.8}(\mu\text{-Cl})_{0.2}(\mathrm{en})_4]\mathrm{Br_3}\cdot 3\mathrm{H_2O}$ (**3**)

Bond distances		Bond distances	
Mo1–Mo2	2.4508(7)		
Mo1–O1	1.955(4)	Mo1–O2	2.09(1)
Mo2–O1	1.947(4)	Mo2–O2	2.10(1)
Mo1–Cl1	2.46(1)	Mo2–Cl1	2.50(2)
O2–C9	1.47(1)	C9–C10	1.49(1)
Mo1–N1	2.232(5)	Mo2–N5	2.236(5)
Mo1–N2	2.303(5)	Mo2–N6	2.257(5)
Mo1–N3	2.254(5)	Mo2–N7	2.278(5)
Mo1–N4	2.242(5)	Mo2–N8	2.223(5)
N1–C1	1.487(8)	N5–C5	1.474(8)
N2–C2	1.481(8)	N6–C6	1.497(8)
N3–C3	1.478(9)	N7–C7	1.474(8)
N4–C4	1.499(8)	N8–C8	1.486(8)
C1–C2	1.516(9)	C5–C6	1.51(1)
C3–C4	1.49(1)	C7–C8	1.49(1)
Bond angles		Bond angles	
Mo2–Mo1–O1	55.7(3)	Mo2–Mo1–O2	50.0(5)
Mo1–Mo2–O1	54.7(3)	Mo1–Mo2–O2	50.8(4)
O1–Mo1–O2	105.6(6)	Mo1–O1–Mo2	69.7(4)
O1–Mo2–O2	105.4(6)	Mo1–O2–Mo2	79.2(5)
Mo1–O2–C9	131(1)	Mo2–O2–C9	132(1)
Mo2–Mo1–N1	103.4(4)	Mo1–Mo2–N5	98.8(4)
Mo2–Mo1–N4	100.0(4)	Mo1–Mo2–N8	101.7(4)
N1–Mo1–N4	156.4(5)	N5–Mo2–N8	158.0(6)

so as to avoid confusion. The crystallographic data for **1**, **2**, and **3** are summarized in Table 1. Interatomic distances and angles are collected in Table 2 for **1**, Table 3 for **2**, and

Table 4 for **3**.

Although the existence of a quadruple bond in dimolybdenum(II) complexes with a d^4–d^4 interaction has been clearly established, a description of the metal-metal bonding in edge-sharing bioctahedral dimolybdenum(III) complexes with a d^3–d^3 interaction is not simple. This is because the interaction of perpendicular lone-pair orbitals on the bridging atoms can invert the order of the energy levels of the δ- and δ^*-orbitals.[25] The Mo(1)–Mo(2) distance in **1** is 2.495(1) Å, and the formal bond order may be three ($\sigma^2\pi^2\delta^2$). The Mo(1)–Mo(2) distances in **2** and **3** are 2.442(1) and 2.4508(7) Å, respectively, and the formal bond order of these complexes may also be three ($\sigma^2\pi^2\delta^2$). The distance is close to those (group A) found in $[Mo_2(\mu\text{-}OH)_2Cl_2(tacn)_2]I_2$ (2.501(3) Å),[2] $K[Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(edta)]$ (2.430(3) Å),[10b] and $[Mo_2(\mu\text{-}OH)(\mu\text{-}H)(\mu\text{-}gly)_2Cl_4]$ (2.353(5) Å)[26] and shorter than those (group B) found in $[Mo_2(\mu\text{-}SEt)_2Cl_4(EtSCH_2CH_2SEt)_2]$ (2.682(1) Å),[27] $[Mo_2(\mu\text{-}SEt)_2Cl_4(Me_2PCH_2CH_2PMe_2)_2]$ (2.712(3) Å),[27] and $[Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4]\cdot C_7H_8$ (2.6293(8) Å).[28] The effective Mo–Mo bond order for group A is reported to be three,[2] and that for group B to be two.[27] It was reported by Cotton et al. that the δ and δ^* levels for group B have very similar energies, the effective Mo–Mo bond order will be two in the structure, based on the fact that the bonding σ and π levels are each doubly occupied; the δ and δ^* levels are both virtually nonbonding.[25]

A comparison of the Mo–N distances in **1** indicates that the trans-influence of μ-O is greater than that of μ-Cl (see Fig. 1, Table 2). The N–C and C–C bond distances of the ethylenediamine ligand in complexes **1** and **3** range between 1.47(1)–1.51(1) Å and 1.47(2)–1.52(2) Å, respectively, falling well within the range of those reported for various metal ethylenediamine complexes.[29] A discussion on the scattered bond distances of the ethylenediamine ligands in complex **2** is impossible, since the standard deviations are rather large.

The complex cations **1**–**3** have *meso* (Λ, Δ) configurations. The configurations are dominant in di-μ-hydroxo dinuclear tetra(ethylenediamine) complexes $[M_2(\mu\text{-}OH)_2(en)_4]^{4+}$ (M = Co^{3+}, Cr^{3+}, Rh^{3+}, Ir^{3+}).[30] The di-μ-chloro complex $[Ni_2(\mu\text{-}Cl)_2(en)_4]^{2+}$ is also of *meso*,[31] and it seems that doubly-bridged dinuclear tetra(ethylenediamine) complexes have *meso* configurations.

Electronic Spectra. The electronic spectra of aqueous solutions of **1**, **2**, **3**, and **4** are shown in Fig. 4. The peak positions of the μ-chloro complex **1** appear at slightly longer wavelengths than the corresponding peak positions of the μ-alkoxo complexes **2**–**4**, and the absorption intensities of **1** at ca. 500 nm is about two-times larger than those of the corresponding bands of the μ-alkoxo complexes **2**–**4**.

In dinuclear molybdenum(III) complexes having bridging ligands, it is characteristic that two absorption bands appear in the region of 600–800 nm, while non-bridged dimeric molybdenum(III) complexes have no absorption bands in this region.[13a] The appearance of peaks in this region in such mononuclear complexes as $[MoCl_3(tacn)]$, $[MoBr_3(tacn)]$, and $[MoI_3(tacn)]$ is ascribed to the weak ligand fields of Cl^-, Br^-, and I^-, respectively. The peak positions in the 600–800 nm region are similar to those of the di-μ-hydroxo molybdenum(III) dimers, $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$,[32] $[Mo_2(\mu\text{-}OH)_2X_2(tacn)_2]^{n+}$ (X = Cl^-, OH^-, H_2O; *n*, dependent on X),[2,4] $[Mo_2(\mu\text{-}OH)_2X(tacn)_2]^{n+}$ (X = HCO_2^-, $CH_3CO_2^-$, CO_3^{2-}; *n*, dependent on X),[2,5] $[Mo_2(\mu\text{-}OH)_2X_2(edta)]^{n-}$ (X = H_2O, NCS^-; *n*, dependent on X),[10] and $[Mo_2(\mu\text{-}OH)_2X(edta)]^-$ (X = $CH_3CO_2^-$, HCO_2^-),[10] and the di-μ-oxo molybdenum(III) dimer $[Mo_2(\mu\text{-}O)_2(edta)]^{2-}$.[9] However, the absorption coefficients of **1**, **2**, **3**, and **4** are much bigger than those of these dimers. The absorption maximum and molar absorption coefficient for **1**, **2**, **3**, **4**, and related complexes are summarized in Table 5.

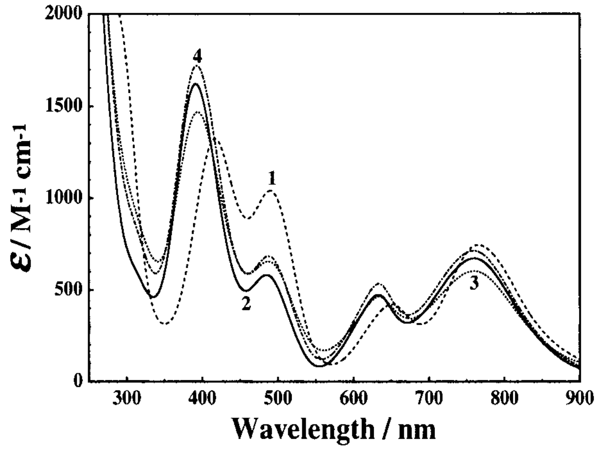


Fig. 4. Absorption spectra of $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**), $[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (**2**), $[Mo_2(\mu\text{-}O)(\mu\text{-}OEt)_{0.8}(\mu\text{-}Cl)_{0.2}(en)_4]Br_3\cdot 3H_2O$ (**3**), $[Mo_2(\mu\text{-}O)(\mu\text{-}OPr)(en)_4]Br_3\cdot 3H_2O$ (**4**).

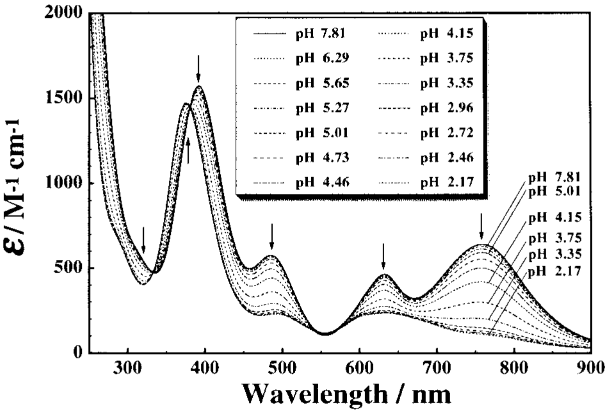
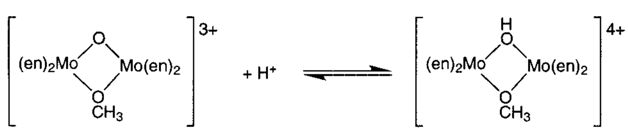


Fig. 5. Spectral change for $[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]^{3+}$ with pH.

Protonation to Bridging Oxygen of the Complexes 1–3. The electronic spectra of the complexes are dependent on the pH. Figure 5 shows the UV-Vis spectra of **2** at pH 2–7. Above pH 6, the spectrum corresponds to the unprotonated oxo-bridged species $[Mo_2(\mu\text{-}O)(\mu\text{-}OMe)(en)_4]^{3+}$. On the other hand, below pH 3, the spectrum corresponds to the hy-



Scheme 1.

Table 5. Electronic Spectral Data of Mo(Ⅲ)-Complexes

Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})					Solvent	Reference
$[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$	766(785)	651 (431)	490 (1092)	418 (1398)		H_2O	a)
$[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$	761(655)	633 (463)	485 (567)	391 (1580)		H_2O	a)
$[Mo_2(\mu\text{-O})(\mu\text{-OEt})_{0.8}(\mu\text{-Cl})_{0.2}(en)_4]^{3+}$	760(627)	634 (461)	485 (633)	394 (1487)		H_2O	a)
$[Mo_2(\mu\text{-O})(\mu\text{-OPr}^n)(en)_4]^{3+}$	759(691)	634 (525)	485 (689)	393 (1718)		H_2O	a)
$[Mo_2(\mu\text{-OH})_2(H_2O)_8]^{4+}$	624(43)	572 (39)		360 (306)		HPTS	32
$[Mo_2(\mu\text{-OH})_2(\mu\text{-CO}_3)(tacn)_2]^{2+}$	735(sh)	630 (71)	450 (sh)	366 (1200)		H_2O	5
$[Mo_2(\mu\text{-OH})_2(\mu\text{-CH}_3CO_2)(tacn)_2]^{3+}$	754(55)	626 (69)		375 (1300)		H_2O	2
$[Mo_2(\mu\text{-OH})_2(\mu\text{-HCO}_2)(tacn)_2]^{3+}$	755(57)	626 (76)		377 (1200)		H_2O	2
$[Mo_2(\mu\text{-OH})_2(OH_2)_2(tacn)_2]^{4+}$	715(sh)	643 (147)	490 (sh)	379 (1400)		H_2O	2
$[Mo_2(\mu\text{-OH})_2Cl_2(tacn)_2]^{2+}$	765(115)	650 (164)	430 (sh)	384 (1200)		H_2O	2
$[Mo_2(\mu\text{-OH})_2(OH)_2(tacn)_2]^{2+}$	640(190)	600 (220)		391 (1200)		H_2O	4
$[Mo_2(\mu\text{-O})_2(H_2O)_2(edta)]^{2-}$	769(25)	617 (40)	435 (48)	358 (880)	287 (1120)	H_2O	9
$[Mo_2(\mu\text{-OH})_2(\mu\text{-CH}_3CO_2)(edta)]^{-}$	750(60)	605 (81)	440 (sh97)	362 (1200)	290 (sh1220)	H_2O	10c
$[Mo_2(\mu\text{-OH})_2(\mu\text{-HCO}_2)(edta)]^{-}$	745(46)	595 (62)	440 (sh75)	360 (767)	290 (1010)	H_2O	10c
$[Mo_2(\mu\text{-OH})_2(NCS)_2(edta)]^{2-}$	750(sh91)	650 (159)	460 (sh421)	383 (2280)	300 (4660)	H_2O	10c
$[Mo_2(\mu\text{-OH})_2(H_2O)_2(edta)]$	690	630 (sh)	570	430 (sh)	365	b)	10c
$[Mo_2(OCMe_3)_6]$		443 (sh700)	406 (1200)	293 (sh1100)	261 (sh2400)	CH_2Cl_2	13a
$[Mo_2(OCMe_2CF_3)_6]$		438 (sh800)	399 (1500)	292 (sh1300)	259 (sh2100)	CH_2Cl_2	13a
$[Mo_2\{OCMe(CF_3)_2\}_6]$		451 (sh700)	413 (1200)	299 (sh1200)	273 (sh2000)	CH_2Cl_2	13a
$[Mo(H_2O)_6]^{3+}$				380 (13.8)	310 (23.2)	HPTS	33
$[MoCl_6]^{3-}$		677 (1.5)	523 (30.6)	419 (41.5)		conc. HCl	34
$[MoCl_3(thf)_3]$			485 (33)	389 (60)	325 (sh135)	EtOH	a)
$[MoCl_3(tacn)]$		684 (16)	421 (130)	355 (246)	315 (410)	CH_3CN	1
$[MoBr_3(tacn)]$		698 (19)	426 (324)	279 (1300)	245 (1000)	CH_3CN	1
$[MoI_3(tacn)]$		732 (66)	469 (132)	385 (5800)	332 (2600)	CH_3CN	1
$[Mo(NCS)_3(tacn)]$					349 (7120)	DMF	1
$[Mo(NH_3)_3(CF_3SO_3)_3]$			595	369	310	b)	8
$[MoCl_2(cyclam)]^{+}$				367 (100)	315 (110)	1 M HCl	6
$[MoCl_2(cyca)]^{+}$				380 (90)	330 (110)	1 M HCl	6
$[MoCl_2([15]aneN_4)]^{+}$				363 (80)	319 (100)	1 M HCl	7

a) This work. b) Diffuse reflectance.

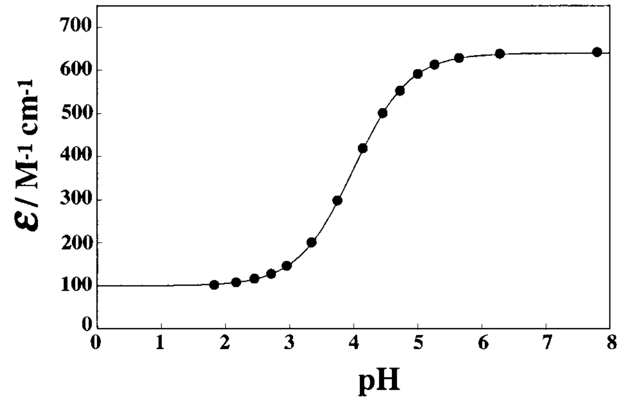


Fig. 6. Plot of apparent molar absorption coefficient of $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$ at 761 nm and pH.

droxo-bridged species $[Mo_2(\mu\text{-OH})(\mu\text{-OMe})(en)_4]^{4+}$, in which the bridging oxygen is protonated. The existence of isosbestic points appearing at 330, 380, 530, and 583 nm indicates the presence of the proton equilibrium of oxo/hydroxo bridging oxygen in **2**, as expressed in Scheme 1. The EDTA complexes $[Mo_2(\mu\text{-OH})_2(CH_3CO_2)(edta)]^{-}$ and $[Mo_2(\mu\text{-OH})_2(NCS)_2(edta)]^{2-}$ also showed spectral a change with the pH, indicating the proton equilibrium of the oxo/hydroxo bridging oxygen.[10c]

The curve of a plot of the apparent absorption coefficients (whose value is the absorbance divided by the analytical concentration of **2**) against pH at 761 nm shows a sigmoid (Fig. 6), and an analysis of the curve gave a value of $pK_a = 4.0$ as the acid dissociation constant of the protonated complex, $[Mo_2(\mu\text{-OH})(\mu\text{-OMe})(en)_4]^{4+}$. The ethoxo-bridged complex $[Mo_2(\mu\text{-O})(\mu\text{-OEt})(en)_4]^{3+}$ and the chloro-bridged complex $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$ also showed spectral changes with the pH. The pK_a values of the complexes $[Mo_2(\mu\text{-OH})(\mu\text{-X})(en)_4]^{4+}$ are 1.2 (X = Cl) and 4.5 (X = OEt). The presence of protonated species of $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$ is negligible at pH values above 4, and the coexistence of the complex will have no influence on the measurement of the pK_a value of $[Mo_2(\mu\text{-O})(\mu\text{-OEt})(en)_4]^{3+}$. A reversible proton transfer is observed in **1**–**3**. The degree of protonation to the bridging oxygen of $[Mo_2(\mu\text{-O})(\mu\text{-X})(en)_4]^{3+}$ depends on another bridging ligand. The basicity of the bridging oxygen of $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$ is very weak compared with those of alkoxo-bridged complexes ($\Delta pK_a \approx 3$). Between the alkoxo-bridged complexes, the basicity of the bridging oxygen of $[Mo_2(\mu\text{-O})(\mu\text{-OEt})(en)_4]^{3+}$ is somewhat stronger than that of $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$. The large difference in the acidity (pK_a values: HCl, completely dissociation; MeOH, 15.1; EtOH, 15.9[35]) has an influence on the basicity of another bridging ligand of oxygen.

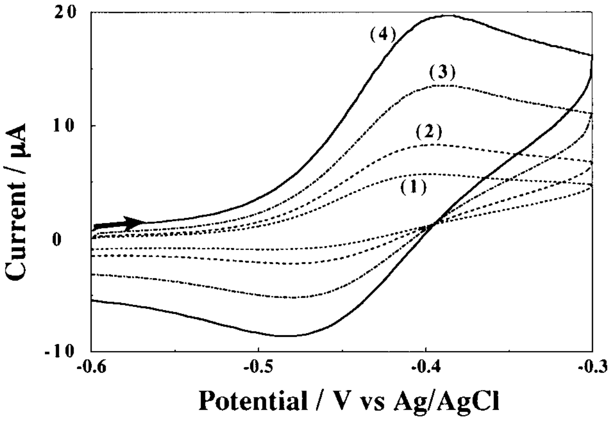


Fig. 7. Cyclic voltammograms of $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$ at glassy carbon electrode in phosphate buffer (pH 7.0) with a scan rate of (1) 100, (2) 200, (3) 500, (4) 1000 mV/s.

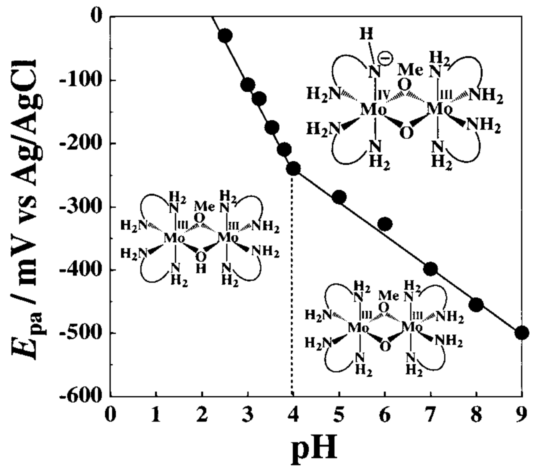


Fig. 8. The plot of the anodic peak potentials (E_{pa}) with pH for $[Mo_2(\mu\text{-O})(\mu\text{-OMe})(en)_4]^{3+}$ at a scan rate of 100 mV/s.

Electrochemistry of Proton-Coupled Electron Transfer from a Coordinated Amino Group and a Bridged Hydroxo Group. Complex **2** indicated a quasi-reversible redox wave in a 0.1 M NaH_2PO_4–NaOH buffer at $E_{1/2} = -0.43$ V vs Ag/AgCl with $\Delta E_p = 82$–98 mV, at scan rates of 100–1000 mV/s in the potential range between −0.6 and −0.3 V (Fig. 7). The value $(\Delta E_p)_{v\to 0}$ obtained by extrapolation of the scanning rate to 0 was 77 mV, indicating a quasi-reversible one-electron transfer. This corresponds to a redox process of $\{Mo^{III}Mo^{III}\}/\{Mo^{IV}Mo^{III}\}$.

Upon a reverse negative potential scan at −0.3 V, the peak current ratio of re-reduction to the oxidation was less than unity, indicating that the oxidative product partially changes into an electrochemically inactive species in solution. This oxidation potential of −0.43 V is negative enough to form an air-oxidized complex of **2**.[36] In fact, this complex undergoes air oxidation in aqueous solutions. The dependence of the oxidation peak potential (E_{pa}) on the pH showed that a proton is involved in electron transfer. A plot of the oxidation peak potential (E_{pa}) against the pH gives two straight lines. In the range of pH above 4.0, the slope of the line is −59 mV/pH, which corresponds to the dissociation of one proton upon one-electron oxidation. One of protons in the amine nitrogens of ethylenediamine ligands coordinating to molybdenum(IV) can dissociate to form amido coordination, as follows (Fig. 8):

$$[(en)_2Mo^{III}(\mu\text{-O})(\mu\text{-OMe})Mo^{III}(en)_2]^{3+}$$
$$\rightleftarrows [(en\text{-}H)(en)_2Mo^{IV}(\mu\text{-O})(\mu\text{-OMe})Mo^{III}(en)_2]^{3+}$$
$$+ H^+ + e^- \ (en\text{-}H = NH_2(CH_2)_2NH^-)$$

A linear relationship with a slope of −118 mV/pH in the pH range below 4.0 indicates the dissociation of two protons upon one-electron oxidation. From the result of the spectral change with the pH, the protonated hydroxo-bridged complex $[(en)_2Mo^{III}(\mu\text{-OH})(\mu\text{-OCH}_3)Mo^{III}(en)_2]^{4+}$ is shown to be the dominant species below pH 4.0. Therefore, the proton dissociations occur at the bridging hydroxo ligand as well as at one amino proton in ethylenediamine ligands (Fig. 8):

$$[(en)_2Mo^{III}(\mu\text{-OH})(\mu\text{-OMe})Mo^{III}(en)_2]^{4+}$$
$$\rightleftarrows [(en\text{-}H)(en)_2Mo^{IV}(\mu\text{-O})(\mu\text{-OMe})Mo^{IV}(en)_2]^{3+}$$
$$+ 2H^+ + e^-$$

The intersection of the two straight lines at pH 4.0 corresponds to the acid dissociation constant (pK_a) of the complex $[(en)_2Mo^{III}(\mu\text{-OH})(\mu\text{-OMe})Mo^{III}(en)_2]^{4+}$. The pK_a value from voltammetric measurements agrees well with that from the absorption spectral change with the pH. A study of the proton-coupled electron transfer for the amine complex includes $[Fe^{II}(tacn)_2]^{2+}/[Fe^{III}(tacn)(tacn\text{-}H)]^{2+}$ (tacn-H = $C_6H_{14}N_3{}^-$)[37] and $[Os^{III}(NH_2CMe_2CMe_2NH_2)_2Cl_2]^+/[Os^{III}(NH_2CMe_2CMe_2NH_2)(NH_2CMe_2CMe_2NH^-)Cl_2]^+$.[38] The oxidative dehydrogenation reaction of amine, which is coordinated to metal ion, has been reported for many metal ions.[39] The deprotonation of amino protons by oxidation of the metal ion is an elementary process that is essential to initiate the oxidative dehydrogenation reaction of the ligand.[40,41]

Complexes **1** and **3** also showed quasi-reversible one-electron oxidation processes, and the oxidation peak potentials depended on the pH of the solution. The small oxidation peak appearing at −0.3 V, near the main oxidation peak, in a cyclic voltammogram of complex **3** at pH 7 may arise from the oxidation of $[Mo_2(\mu\text{-O})(\mu\text{-Cl})(en)_4]^{3+}$ because the complex was an 8:2 mixture of the oxo- and ethoxo-bridged complex and the oxo- and chloro-bridged complex (Fig. 9). The intersection of the two straight lines in a plot of E_{pa} for the main oxidation peak against pH gave a value of $pK_a = 4.2$ as an acid dissociation constant of the protonated complex, $[Mo_2(\mu\text{-OH})(\mu\text{-OEt})(en)_4]^{4+}$. A similar plot for complex **1** in the pH range from 1 to 12 gave only one straight line with a slope of −59 mV/pH due to the strong acidity of $[Mo_2(\mu\text{-OH})(\mu\text{-Cl})(en)_4]^{4+}$, in which the pK_a value was found to be 1.2 from spectral measurements. All of the complexes **1**–**3** studied here exhibit a proton-coupled electron transfer that involves deprotonation from an amino proton of ethylenediamine ligands on the oxidation:

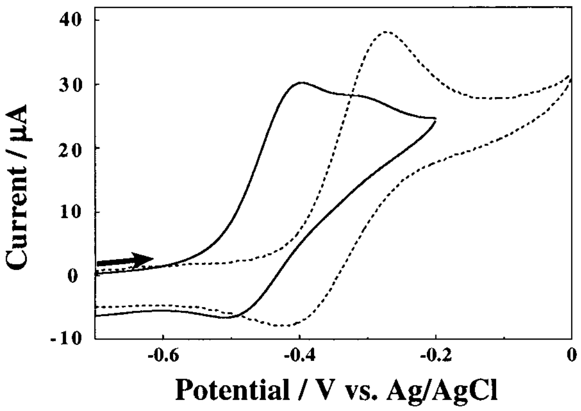


Fig. 9. Cyclic voltammograms of $[Mo_2(\mu\text{-}O)(\mu\text{-}OEt)_{0.8}(\mu\text{-}Cl)_{0.2}(en)_4]^{3+}$ (solid line) and $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4]^{3+}$ (dotted line) at glassy carbon electrode in phosphate buffer (pH 7.0) with a scan rate of 100 mV/s.

$$\begin{aligned}&[(en)_2Mo^{\mathrm{III}}(\mu\text{-}O)(\mu\text{-}X)Mo^{\mathrm{III}}(en)_2]^{3+}\\ &\rightleftarrows [(en\text{-}H)(en)_2Mo^{\mathrm{IV}}(\mu\text{-}O)(\mu\text{-}X)Mo^{\mathrm{III}}(en)_2]^{3+}\\ &\quad + H^+ + e^-\end{aligned}$$

The oxidation peak potential (E_{pa}) of the alkoxo-bridged complexes (X = OMe, OEt) is about 120 mV more negative than that of the chloro-bridged complex (X = Cl); therefore, the alkoxo-bridged complexes are more easily oxidized than the chloro-bridged complex. The acidity of the bridging hydroxo and ethylenediamine ligands is strengthened by oxidation of the molybdenum center, and deprotonation then occurs from these ligands upon oxidation. It has been proved experimentally for the first time that the redox of the Mo–O–Mo moiety is coupled with proton transfer.

Conclusion

Four novel dimeric molybdenum(III) ethylenediamine complexes with μ-oxo-μ-chloro or μ-oxo-μ-alkoxo bridges $[Mo_2(\mu\text{-}O)(\mu\text{-}X)(en)_4]^{3+}$ (X = Cl, OMe, OEt, OPr^n) were synthesized from the mononuclear complex $[MoCl_3(thf)_3]$, and the X-ray structures were determined, except for X = OPr^n.

These oxo-bridged complexes change to the hydroxo-bridged complexes in acidic solutions. Deprotonation of the coordinated amines was observed upon oxidation by a cyclic voltammetric measurement (pH 1.0–10.0) of complexes. This is the first example of proton-coupled electron-transfer of molybdenum complexes.

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