Oxo- and Alkoxo-Bridged Dimeric Molybdenum(III) Ethylenediamine Complexes

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Oxo- and alkoxo-bridged dimeric molybdenum(III) ethylenediamine complexes, $[Mo_2(\mu\text{-}O)(\mu\text{-}R)(en)_4]^{3+}$ (R = OMe (**3**); R = OEt (**4**)) were synthesized from the mononuclear complex $[MoCl_3(thf)_3]$, and were characterized structurally, spectroscopically, and electrochemically, where the methoxy- and ethoxy-bridges were introduced by using methanol and ethanol as the solvent, respectively. The electronic spectra of **3** and **4** have characteristic peaks in visible and near infrared region, and the addition of acid causes a dramatic decrease of the peak heights.

We have recently reported the oxo- and chloro-bridged dinuclear molybdenum(III) complex, $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4]^{3+}$ (**1**) obtained from $[MoCl_3(thf)_3]$ (**2**) and ethylenediamine in DMF.[1] The use of either methanol or ethanol in stead of DMF resulted in the formation of oxo- and alkoxo-bridged dimeric molybdenum(III) ethylenediamine complexes, $[Mo_2(\mu\text{-}O)(\mu\text{-}R)(en)_4]^{3+}$ (R = OMe (**3**); R = OEt (**4**)). A variety of molybdenum(III) complexes with terminal and/or bridging alkoxo ligands have been reported.[2] However, neither methoxo nor ethoxo bridged dinuclear Mo(III) complexes have been reported so far.

The compound $\mathbf{3}\cdot Br_{2.2}Cl_{0.8}\cdot 3H_2O$ (**3'**) was synthesized under a dinitrogen atmosphere. Anhydrous ethylenediamine (en/Mo = 6) was added to **2** (5.78 mmol) in 1.0 M $LiBr{\cdot}H_2O$ methanol solution (20.2 mL). Then, the mixture was heated at ca. 50 °C for 3 h, cooled to room temperature, and stored in a freezer overnight. Green precipitate deposited was filtered and washed with ethanol. Recrystallization from water by the addition of ethanol gave green crystals of **3'**: yield 5.9% based on **1**. 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, 3.85%. The μ-oxo-μ-ethoxo complex, $\mathbf{4}\ Br_3{\cdot}3H_2O$ (**4'**), was also prepared by the similar procedure to the synthesis of **3'** using ethanol as the solvent.[3]

The X-ray analyses of **3'** and **4'** revealed the existence of μ-oxo-μ-methoxo and μ-oxo-μ-ethoxo dinuclear molybdenum cores, respectively, and the coordination of four ethylenediamine molecules to each dinuclear molybdenum cores.[4] The cation of **3'** is shown in Figure 1. The Mo1–Mo2 distances (**3'**, 2.442(1); **4'**, 2.4512(8) Å)[4] are close to those in $\mathbf{1}\cdot(S_2O_6)Cl\cdot 3H_2O$ (2.495(1) Å),[1] $K[Mo_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(edta)]$ (2.430(3) Å),[5] and $[Mo_2(\mu\text{-}OH)_2Cl_2(tacn)_2]I_2$ (2.501(3) Å).[6]

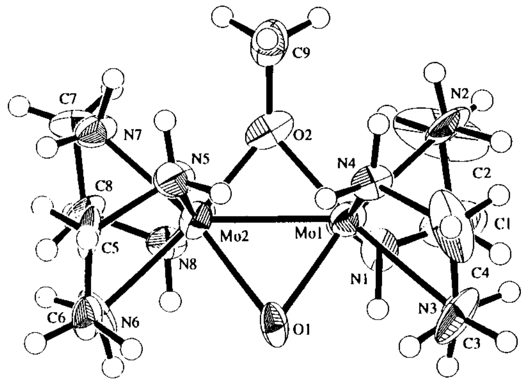

Figure 1. Perspective view of the cation in **3'**. Selected atomic distances(Å) and angles(°): Mo1-Mo2, 2.442(1); Mo1-O1, 2.13(1); Mo1-O2, 1.93(1); Mo1-N1, 2.21(1); Mo1-N2, 2.26(2); Mo1-N3, 2.35(2); Mo1-N4, 2.20(1); Mo2-O1, 2.15(1); Mo2-O2, 1.90(2); Mo2-N5, 2.24(2); Mo2-N6, 2.24(1); Mo2-N7, 2.19(2); Mo2-N8, 2.28(2); O2-C9, 1.48(2); O1-Mo1-O2, 105.6(6); O1-Mo2-O2, 105.4(6); Mo1-O1-Mo2, 69.7(4); Mo1-O2-Mo2, 79.2(5).

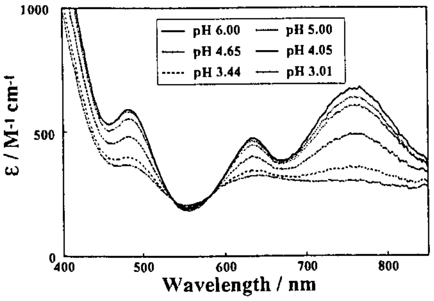

Figure 2. Electronic spectra of **3'** at different pH values.

Electronic spectrum of **3'** in water is shown in Figure 2: each λ_{max} (ε-value), 391(1580), 485(567), 633(463), 761(655)), is similar to that of the μ-oxo-μ-chloro complex **1**. Addition of hydrochloric acid to the aqueous solution of **3** and **1** causes a dramatic decrease of the peak heights at 450–900 nm region and addition of ammonia water to the acidified solutions recovers the high absorbancy, respectively. The spectrum of **4** also behaves similarly on the addition of acids and alkalines. Therefore proton-addition to the μ-O moieties is most probable (eq 1: X = Cl (**1**); OMe (**3**); OEt (**4**)).

$$[Mo_2(\mu\text{-}O)(\mu\text{-}X)(en)_4]^{3+} + H^+ \rightleftharpoons [Mo_2(\mu\text{-}OH)(\mu\text{-}X)(en)_4]^{4+} \qquad (1)$$

The presence of μ-X gives an influence on the protonation to μ-O, and the μ-oxo-μ-alkoxo complexes: the alkoxo complexes, **3** and **4**, are much more sensitive to acids than the μ-oxo-μ-chloro complex **1** is. Deprotonation of the di-μ-hydroxo dinuclear Mo(III) complex $[Mo_2(\mu\text{-}OH)_2(OAc)(edta)]^-$ (**5**) has been reported:[5c] addition of alkaline solution to **5** gives larger peaks, which indicates dissociation of H^+ from one of the di-μ-hydroxo bridges (see eq 2).

$$[Mo_2(\mu\text{-}OH)_2(OAc)(edta)]^- \rightleftharpoons [Mo_2(\mu\text{-}OH)(\mu\text{-}O)(OAc)(edta)]^{2-} + H^+ \qquad (2)$$

The μ-oxo-μ-hydroxo complex is negatively charged (2–) and may have much higher tendency to receive the positively charged species H^+ than those of **1**, **3**, or **4** having positive charges (3+) do. However, another di-μ-hydroxo dinuclear Mo(III) complex $[Mo_2(\mu\text{-}OH)_2Cl_2(tacn)_2]^{2+}$ has positive charge.[6] Proton addition to alkoxo bridges is another possibility, and much research will be required to clarify the factor for proton addition and dissociation.

Figure 3 shows cyclic voltammograms of **3'** in phosphate buffer solution (pH = 7.0) at different scan rates. The peak potential separation extrapolated to the scan rate of zero is close to 60 mV, indicating that the oxidation is one-electron process. A plot of the formal redox potential vs pH yields two straight lines with the slopes of about 60 mV and 120 mV. The pH at the intersection of two lines is 4.3 which corresponds to the pK_a value of the protonated species of **3**.

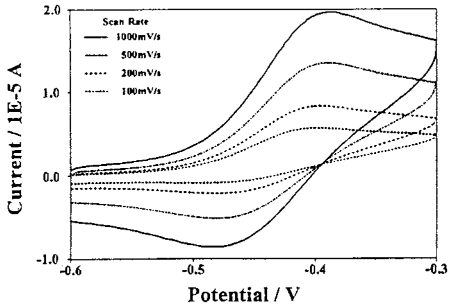

Figure 3. Cyclic voltammograms of **3'** in phosphate buffer solution (pH=7.0) at different scan rates.

We have also succeeded in the preparation of the other μ-oxo-μ-alkoxo complexes using alcoholic solution other than methanol and ethanol, and the characterization is in progress.

References and Notes

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2 For example, a) Mo(III) dimer with terminal alkoxo groups: M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *Organometallics*, **1**, 251 (1982); M. H. Chisholm, I. P. Parkin, J. C. Huffman, E. M. Lobkovsky, and K. Folting, *Polyhedron*, **10**, 2839 (1991); T. M. Gilbert, A. M. Landes, and R. D. Rogers, *Inorg. Chem.*, **31**, 3438 (1992). b) Mo(III) dimer with terminal and bridging alkoxo groups: M. H. Chisholm, K. Folting, J. C. Huffman, and J. J. Koh, *Polyhedron*, **8**, 123 (1989); M. H. Chisholm, D. M. Hoffman, J. McC. Northius, and J. C. Huffman, *Polyhedron*, **16**, 839 (1997). c) Mononuclear and polynuclear Mo(III) complexes with methoxy, ethoxy, or other groups: F. A. Cotton, B. Hong, and M. Shang, *Inorg. Chem.*, **32**, 4876 (1993); M. H. Chisholm, C. E. Hammond, M. Hampden-Smith, J. C. Huffmann, and W. G. Van der Sluys, *Angew. Chem., Int. Ed. Engl.*, **26**, 904 (1987); A. Proust, F. Robert, P. Gouzerh, Q. Chen, and J. Zubieta, *J. Am. Chem. Soc.*, **119**, 3523 (1997).

3 Found: C, 15.71; H, 5.27; N, 14.71%. Calcd for $C_{10}H_{43}N_8O_5Mo_2Br_3$: C, 15.26; H, 5.51; N, 14.24%. Addition of NaOEt is required for the preparation of pure sample: otherwise the contamination of the oxo- and chloro-bridged complex, $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4]^{3+}$ (**1**) will be recognized.

4 Crystal data for **3'**: Formula $Mo_2Br_{2.2}Cl_{0.8}O_5N_8C_9H_{41}$, MW = 737.50, monoclinic, space group *Cc*(#9), a = 17.591(2) Å, b = 15.294(2) Å, c = 10.120(3) Å, V = 2541.4(8) $Å^3$, Z = 4, D_c = 1.927 g cm^{-3}, $R(R_w)$ = 0.067(0.099) for 2366 reflections ($I > 3.0\ \sigma(I)$). Crystal data for **4'**: Formula $Mo_2Br_3O_5N_8C_{10}H_{43}$, MW = 787.09, monoclinic, space group $P2_1/c$ (#14), a = 10.098(2) Å, b = 14.962(3) Å, c = 18.085(3) Å, V = 2682(1) $Å^3$, Z = 4, D_c = 1.949 g cm^{-3}, $R(R_w)$ = 0.046(0.076) for 3666 reflections ($I > 3.0\ \sigma(I)$). Selected atomic distances(Å) and angles(°) in **4'**: Mo1–Mo2, 2.4515(9); Mo1–O1, 1.961(5); Mo1–O2, 2.218(5); Mo1–N1, 2.232(6); Mo1–N2, 2.290(6); Mo1–N3, 2.247(6); Mo1–N4, 2.246(6); Mo2–O1, 1.948(5); Mo2–O2, 2.242(5); Mo2–N5, 2.230(6); Mo2–N6, 2.259(6); Mo2–N7, 2.282(6); Mo2–N8, 2.227(6); O2–C9, 1.428(5); C9–C10, 1.41(1); O1–Mo1–O2, 108.0(2); O1–Mo2–O2, 107.6(2); Mo1–O1–Mo2, 77.7(2); Mo1–O2–Mo2, 66.7(1).

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