An Oxo- and Chloro-Bridged Dimeric Molybdenum(III) Ethylenediamine Complex

Shunji Kiyoda,* Haruo Akashi,† Tsukio Ohtani,†† and Takashi Shibahara*††
Research Institute for Advanced Science and Technology, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 599-8570
†*Research Institute of Natural Sciences, Okayama University of Science, Ridai-cho, Okayama 700-0005*
††*Department of Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005*

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An oxo- and chloro-bridged dimeric molybdenum(III) ethylenediamine complex, $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**) was synthesized from the mononuclear complex $[MoCl_3(thf)_3]$, and was characterized structurally and spectroscopically for the first time. 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 trans influence of μ-O on the Mo-N bond lengths proved to be greater than that of μ-Cl.

The number of mononuclear[1-5] or dinuclear molybdenum(III) amine complexes is limited and, to our knowledge, only the following amine complexes have been reported: di-μ-hydroxo bridged tacn complexes $[Mo_2(\mu\text{-}OH)_2X_2(tacn)_2]^{2+}$ (tacn = 1,4,7-triazacyclononane; X = Cl,[6] Br[7]) and $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(tacn)_2]^{3+}$;[6] a μ-bromo-μ-hydroxo bridged tacn complex $[Mo_2(\mu\text{-}Br)(\mu\text{-}OH)Br_2(tacn)_2]^{2+}$;[7] di-μ-hydroxo bridged edta complexes $[Mo_2(\mu\text{-}OH)_2(edta)(L)]^n$ (L = $(H_2O)_2$, n = 0; L = OAc, n = 1-; L = $(NCS)_2$, n = 2-; L = O_2CH, n = 1-) and related hedta complexes;[8] and a di-μ-oxo bridged edta complex $[Mo_2(\mu\text{-}O)_2(edta)(H_2O)_2]^{2-}$.[9]

To date, several dinuclear molybdenum(IV or V) complexes with both oxo- and chloro-bridges have been reported.[10,11] Also, many dinuclear molybdenum(III) complexes with a variety of bridging groups are known: for example, complexes with $Mo_2(\mu\text{-}OH)_2$,[12] $Mo_2(\mu\text{-}O)_2$,[13] $Mo_2(\mu\text{-}Cl)_3$,[14] $Mo_2(\mu\text{-}Br)_3$,[14] $Mo_2(\mu\text{-}SEt)_2$,[15] $Mo_2(\mu\text{-}SEt)_3$,[16] $Mo_2(\mu\text{-}O)$,[17] $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)$,[18] $Mo_2(\mu\text{-}OH)(\mu\text{-}H)$,[19] $Mo_2(\mu\text{-}SH)(\mu\text{-}SCH_3)_2$,[20] and Mo_2 (no bridging groups)[21] cores.[22] Here, we report the synthesis, X-ray structure and characterization of a dimeric molybdenum(III) ethylenediamine complex $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**). This is the first example of an oxo- and chloro-bridged dimeric molybdenum(III) complex.

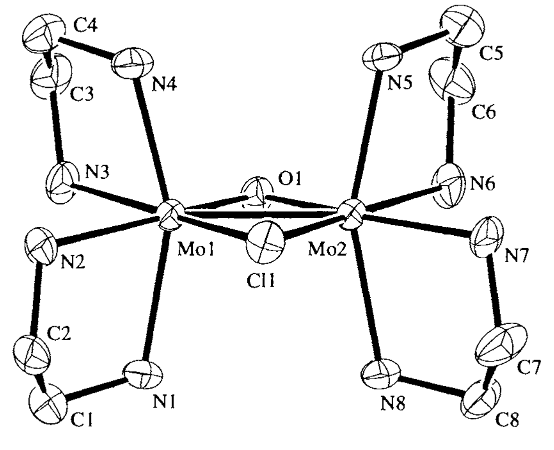

Figure 1. Perspective view of the cation in $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**). Selected atomic distances(Å) and angles(°): Mo1-Mo2, 2.495(1); Mo1-Cl1, 2.428(2); Mo2-Cl1, 2.436(2); Mo1-O1, 1.928(6); Mo2-O1, 1.921(6); Mo1-N1, 2.234(7); Mo1-N2, 2.276(7); Mo1-N3, 2.236(7);Mo1-N4 2.205(7); Mo2-N5 2.230(7); Mo2-N6 2.216(8); Mo2-N7, 2.277(7); Mo2-N8, 2.231(7); Cl1- Mo1-O1, 108.7(2); Cl1-Mo2-O1, 108.7(2); Mo1-Cl1-Mo2, 61.73(6); Mo1-O1-Mo2, 80.8(2).

The compound **1** was synthesized under a dinitrogen atmosphere. Ethylenediamine (5.0 cm^3) was added to a conical flask cooled in an ice-bath containing $[MoCl_3(thf)_3]$ (5.19 g)[23] dissolved in DMF (62 cm^3). Then, the solution was stirred at room temperature. After several minutes the color of the solution turned from red-brick 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: yield 3.89 g. This powder was dissolved in aq. $Na_2S_2O_6$ 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 0.51 g (12%).[24]

The X-ray analysis[25] of **1** revealed the existence of a μ-oxo-μ-chloro dinuclear molybdenum core and coordination of four ethylenediamine molecules to the molybdenum atoms (Figure 1). Although the existence of a quadruple bond in dimolybdenum(II) complexes with d^4-d^4 interactions has been well established, a description of the metal-metal bonding in edge-sharing bioctahedral dimolybdenu(III) complexes with d^3-d^3 interactions 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 δ- and δ*-orbitals.[26] 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 distance is close to those (group A) found in $[Mo_2(\mu\text{-}OH)_2Cl_2(tacn)_2]I_2$ (2.501(3)

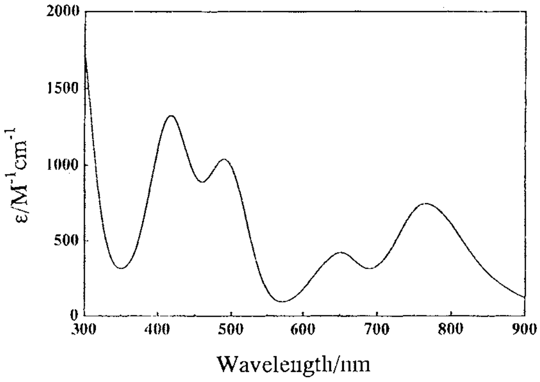

Figure 2. The electronic spectrum of $[Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4](S_2O_6)Cl\cdot 3H_2O$ (**1**) in water.

Å),[6] K[$Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(edta)$] (2.430(3) Å),[8] and [$Mo_2(\mu\text{-}OH)(\mu\text{-}H)(\mu\text{-}gly)_2Cl_4$] (2.353(5) Å),[19] and shorter than those (group B) found in [$Mo_2(\mu\text{-}SEt)_2Cl_4(EtSCH_2CH_2SEt)_2$] (2.682(1) Å),[15] $Mo_2(\mu\text{-}SEt)_2Cl_4(Me_2PCH_2CH_2PMe_2)_2$] (2.712(3) Å),[15] and [$Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4$]·$C_7H_8$ (2.6293(8) Å).[18] The effective Mo-Mo bond order for group A is reported as three,[6] and that for group B as two.[15] Also, the comparison of Mo-N distances in **1** indicates that the trans influence of μ-O is greater than that of μ-Cl (see Figure 1).

The electronic spectrum of **1** is shown in Figure 2.[27] Peak positions in the visible region 600-800 nm are similar to those of di-μ-hydroxo Mo(III) dimers.[6,8] However, the epsilon values are much larger in the visible region than those of the dimers. The appearance of absorption in the spectrum of **1** at longer wavelengths in the visible region and the diamagnetism of **1** are in accordance with the short Mo-Mo distance.

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24 Anal. (Calcd for $Mo_2Cl_2S_2O_{10}N_8C_8H_{38}$): Cl, 9.5(9.67); S, 8.7(8.74); C, 12.96(13.10); H, 5.31(5.22); N, 15.10(15.28)%. Recrystallization from water to give [$Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(en)_4$]-$Cl_3\cdot 3H_2O$ (**1a**) was also possible by the addition of ethanol. Formation of the complex **1a** was confirmed by comparison of the electronic spectrum with that of **1**.

25 Crystal data for **1**: Formula $Mo_2Cl_2S_2O_{10}N_8C_8H_{38}$, Mw = 733.34, orthorhombic system, space group $Pca2_1$ (#29), a = 18.760(5) Å, b = 13.537(4) Å, c = 10.070(4) Å, V = 2557(1) $Å^3$, Z = 4, Dc = 1.905 gcm^{-3}, $R(Rw)$ = 0.047(0.068) for 2678 reflections ($I > 2.00\sigma(I)$).

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27 λmax, nm (ε(dimer), $mol^{-1}dm^3cm^{-1}$): 766(785), 651(431), 490(1092), 418(1398), 290sh(2081). The peaks disappeared rapidly on exposure to air.