Synthesis and X-ray Analysis of Mn–Mo Mixed Metal Oxide Cluster with Cubic Framework

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A reaction of the dinuclear oxometalate $[Bu^n_4N]_2[Mo_2O_7]$ and $(tacn)MnCl_3$ (tacn = 1,4,7-triazacyclononane) in water afforded a new cubic type Mn–Mo mixed metal oxide cluster of $[\{(tacn)Mn\}_2Mo_4O_{16}]\cdot 4H_2O$ which has a moderate bleaching ability towards pinacyanol chloride dye.

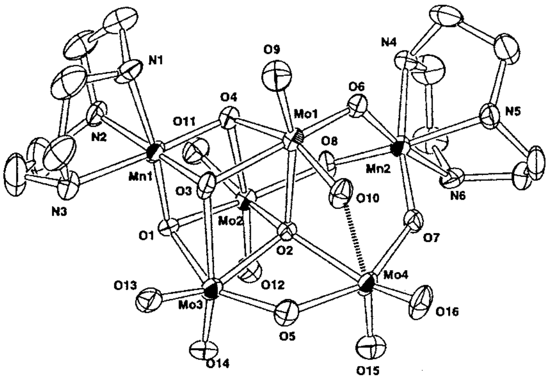

Figure 1. ORTEP drawing of complex **1**. All hydrogen atoms and crystalline water molecules were omitted for clarity. Selected distances (Å) and angles (deg): Mo1–O2: 2.344(7), Mo1–O3: 2.056(6), Mo1–O4: 2.100(6), Mo2–O1: 2.122(6), Mo2–O2: 2.116(6), Mo2–O4: 2.360(7), Mo3–O1: 2.085(6), Mo3–O2: 2.120(6), Mo3–O3: 2.369(7), Mo4–O2: 2.124(6), Mo4–O5: 2.035(6), Mo4–O7: 1.897(6), Mn1–O1: 1.875(6), Mn1–O3: 1.832(7), Mn1–O4: 1.814(6), Mn1–N1: 2.050(9), Mn1–N2: 2.045(8), Mn1–N3: 2.062(9), Mn2–O6: 1.846(7), Mn2–O7: 1.815(6), Mn2–O8: 1.835(7), Mn2–N4: 2.056(7), Mn2–N5: 2.054(8), Mn2–N6: 2.024(8), Mn1–O1–Mo2: 102.2(3), Mn1–O1–Mo3: 103.4(3), Mo2–O1–Mo3: 103.8(3), Mo1–O2–Mo2: 105.5(2), Mo1–O2–Mo3: 106.2(3), Mo1–O2–Mo4: 99.9(3), Mo2–O2–Mo3:102.8(3), Mo2–O2–Mo4:141.1(3), Mo3–O2–Mo4: 96.6(2), Mo1–O4–Mo2: 105.5(2), Mo3–O5–Mo4: 109.9(3).

Organometallic oxide clusters with cubic and incomplete cubic frameworks are useful as homogeneous and heterogeneous catalysts in the oxidation and metathesis of unsaturated hydrocarbons.[1] We have synthesized several organometallic oxide clusters with the latter frameworks, for example the triple cubic $[(Cp^*Rh)_4Mo_4O_{16}]$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[2] the incomplete double cubic $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$,[3] the double bookshelf $[(Cp^*Rh)_2Mo_6O_{20}(OMe)_2]^{2-}$ type oxide clusters and so on.[4] These clusters are formed by the condensation of oxometalate anions on the Lewis acidic Cp*Rh moiety, which is able to provide three coordination sites for the condensation. We are extending our synthetic method to the preparation of oxide clusters with a (tacn)Mn group that also has three available sites and functions as an oxidizing agent.[5] Here we report the synthesis, structure, and preliminary results involving oxidation catalysis of a new Mn–Mo mixed metal cluster, $[\{(tacn)Mn\}_2Mo_4O_{16}]\cdot 4H_2O$ (**1**).

Cluster **1** was synthesized under aerobic conditions as follows:[6] To a suspension of $[Bu^n_4N]_2[Mo_2O_7]$ (272 mg, 0.344 mmol) in H_2O (20 cm^3) was slowly added a solution of $(tacn)MnCl_3$ (100 mg, 0.344 mmol) in H_2O (10 cm^3). The red brown suspension was stirred for 20 min at room temperature, and then for 1 h at 95 ˚C. The mixture was cooled to room temperature, the unreacted $[Bu^n_4N]_2[Mo_2O_7]$ was filtered off and the red filtrate was allowed to stand for several days to give red crystals of **1** (yield: 41 mg, 22% based on Mn).

X-ray analysis[7] of **1** reveals that it is composed of a cubic framework consisting of one Mn(IV), three Mo(VI) (Mo1, Mo2, and Mo3) ions and four oxygen atoms. It also has two valley sites and an incomplete cubic framework formed by three Mo(VI) (Mo1, Mo3, and Mo4) ions and four oxygen atoms. One (tacn)Mn at the corner of the cube is bound to a triply bridging oxygen (O1, O3, and O4) and the other to the doubly bridging oxygens (O6, O7, and O8). Although each Mn atom coordinates to two different kinds of oxygen atoms separately, all of the Mn–O bond lengths except for Mn1–O1 (1.875(6) Å) are within 1.815(6)–1.846(6) Å. The Mo–O bonds can be classified into four different categories. The first is a terminal Mo–O bond with bond lengths of 1.698(8)–1.728(6) Å, which has strong double bond character. The second has a doubly bridging oxygen atom, which retains double bond character with respect to the Mo atom (bond lengths of 1.843(6)–1.897(6) Å).

The third type has a triply bridging oxygen atom and their bond lengths are within 2.056(6)–2.369(7) Å, and finally, the fourth has a quadruply bridging oxygen atom (bond lengths of 2.116(6)–2.344(7) Å). Mo4 has a weak interaction with O10 with a distance of 2.471(7) Å. This weak bond is similar to the secondary bonding observed with some M–halide bonds.[8] The Mn–N bonds respect to both Mn1 and Mn2 ranging in 2.024(8)–2.062(9) Å, which are reasonable bond lengths between Mn (IV) and N (tacn) atoms.[9]

The bond angles ∠Mn–O–Mo, which are formed by the coordination of (tacn)Mn2 to the oxygen atoms of Mo=O, are in the range of 128.1(4)–140.8(4)°. This indicates that these oxygen atoms have sp^2 hybridization character which is also supported by the Mo–O bond length mentioned above. Other ∠M–O–M angles are around 100° reflecting tetrahedral arrangement of the corresponding oxygen atoms, except very distorted tetrahedral O2 makes an intriguing bond angle of ∠Mo2–O2–Mo4 (141.1(3)°).

We examined catalytic bleaching ability of cluster **1** towards pinacyanol chloride dye (PC dye) under heterogeneous conditions in water at 25 °C.[10] For comparison, the newly prepared Rh–Mo cluster, $[(Metacn)_2Rh_2(\mu\text{-}MoO_4)_3]\cdot 17H_2O$ (**2**)[11] (Metacn = *N,N',N''*-trimethyl-1,4,7-triazacyclononane) was also examined. In the reaction using **1** the blue color of the PC dye disappeared in 6 h. With **2** or without any catalyst a reaction time of 48 h was needed for complete decoloration. Preliminary results show that cluster **1** can be used as a mild heterogeneous bleaching catalyst.

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6 When the synthetic reaction was carried out under an argon atmosphere, cluster **1** was not formed: the aerobic conditions are required for the oxidation of Mn(III) to Mn(IV) to form **1**.

7 Crystal data for **1**: $C_{12}H_{38}N_6Mn_2Mo_4O_{20}$ (fw = 1080.10: tetrahydrate), black-red plate crystal (the crystal size, 0.30 × 0.44 × 0.06 mm), orthorhombic, *Pbca* (#61), a = 23.245(4) Å, b = 20.189(4) Å, c = 12.608(8) Å, V = 5916(5) Å^3, Z = 8, D_{calc} = 2.425 g/cm^3, μ(Mo Kα) = 25.62 cm^{-1}, measured reflections = 9415, observed reflections = 3848, R = 0.047, R_w = 0.052, G.O.F. = 1.22. Intensity data were measured on a Rigaku AFC7S diffractometer using ω–2θ scan technique with graphite monochromated MoKα radiation (λ = 0.71069 Å). 9413 unique reflections within $4 \le 2\theta \le 60^\circ$ were collected. The data were corrected for Lorentz and polarization effects. No decay correction was applied. The structure was solved and refined by using the *teXsan* programs. Anal. Calcd. for $C_{12}H_{38}N_6Mn_2Mo_4O_{20}$ (tetrahydrate): C, 13.34; H, 3.55; N, 7.78; Mn, 10.17%. Found: C, 13.55; H, 3.52; N, 7.78; Mn, 10.0% (Mn content was confirmed by inductively coupled plasma-atomic emission spectroscopy: its value has three significant digits). IR spectrum (KBr): ν (M–O) consists of at least 8 strong peaks (922, 876, 837, 814, 797, 756, 681, and 655 cm^{-1}).

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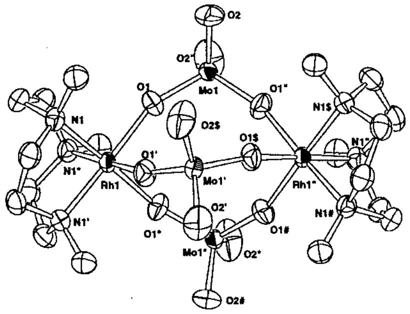
10 Reaction conditions: hydrogen peroxide (15 μmol), PC dye (15 μmol), and the catalyst (1.5 μmol) in water (10 mL) at 25 °C.

11 Cluster **2** was synthesized from the reaction of (Metacn)$RhCl_3$ with $Na_2MoO_4 \cdot 2H_2O$ in water (28% yield). The molecular structure of **2** is composed of two (Metacn)Rh(III) units coordinated to triply bridged $[MoO_4]^{2-}$ moieties as shown below. A similar structure was suggested for $[(\text{Metacn})_2Fe_2(\mu\text{-}MoO_4)_3]$ via IR spectroscopy[12] and recently both $[(\text{Metacn})_2Cr_2(\mu\text{-}MoO_4)_3]$ and $[(\text{Metacn})_2Co_2(\mu\text{-}MoO_4)_3]$ have been synthesized and characterized by the Hayashi and Uehara group.[13] Crystal data for **2**: $C_{18}H_{76}N_6Mo_3O_{29}Rh_2$ (fw = 1334.46: heptadecahydrate), yellow block crystal (the crystal size, 0.50 × 0.50 × 0.40 mm), trigonal, $R\bar{3}c$ (#167), a = 14.576(2) Å, c = 38.959(6) Å, V = 7168(1) Å^3, Z = 6, D_{calc} = 1.855 g/cm^3, μ(Mo Kα) = 15.28 cm^{-1}, measured reflections = 4981, observed reflections = 1942, R = 0.030, R_{w} = 0.048, G.O.F. = 1.70. Anal. Calcd for $C_{18}H_{54}N_6Mo_3O_{18}Rh_2$ (hexahydrate) (the sample was dried under vacuum for 48 h): C, 19.03; H, 4.79; N, 7.40%. Found: C, 19.00; H, 4.74; N, 7.39%. IR spectrum (KBr): ν (M–O) 900s, 855sh, 800s, and 750s cm^{-1}.



ORTEP drawing of complex **2**. All hydrogen atoms and crystalline water molecules were omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1–O1: 2.029(3), Mo1–O1: 1.757(2), Mo1–O2: 1.732(3), O1–Rh1–O1’: 88.9(1), O1–Rh1–N1: 93.4(1), O1–Rh1–N1’: 91.9(1), O1–Rh1–N1”: 177.7(1).

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