Preparation of a Binuclear Oxo(tropolonato)molybdenum(V) Complex and Its Spectroscopic Properties and Crystal Structure

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To a solution of tropolone (**1**) in ethanol was added a solution of $Mo_2O_4{}^{2+}$ in 2 M HCl. The mixture was stirred at 25 °C for 15 min yielding the title new complex, $[Mo_2O_4(trop)_2]$ (**2**), with two molecules of ethanol as ligands.

The chemistry of molybdenum(V) complexes with chelate organic ligands (e.g., amino and organic acids and dithiocarbamates) has been studied to a considerable extent, and the molecular structures and properties for a number of compounds of this type have been well documented. Furthermore, in 2002 M. Cindrić and his co-workers reported the crystal structures of binuclear oxomolybdenum(V) complexes **3**[1] and **4**[1] with two isomers: ethyl 4-hydroxy-3-[3-(4-methoxyanilino)-2-butenoyl]-2*H*-pyran-2-oxo-6-carboxylate (**a**) and ethyl 4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-2-(4-methoxyanilino)-4-oxo-2-butenoate (**b**) as ligands, along with their syntheses and properties. The general formula of **3** and **4** is $[Mo_2O_4L_2D_2]$, where ligand L is deprotonated isomer **a** (for **3**) or **b** (for **4**) and ligand D is methanol (for both **3** and **4**). On the other hand, the crystal structures of a *cis*-dioxobis(tropolonato)molybdenum(VI) complex, $[MoO_2(trop)_2]$,[2] and a binuclear oxo(tropolonato)molybdenum(VI) complex, $(n\text{-}Bu_4N)_2[Mo_2O_6(trop)_2]$,[3] have been reported, however, nothing has so far been established in terms of the crystal structure of the title complex, $[Mo_2O_4(trop)_2]$ (**2**). Recently, our interest has been focused on the preparation of complex **2** and, further, its characteristic properties and crystal structure compared with those of complexes **3** and **4**, whose coordination geometry for each molybdenum atom of the $[O{=}Mo(\mu\text{-}O)_2Mo{=}O]^{2+}$ centers coincided with that of **2**.

A solution of $Mo_2O_4{}^{2+}$ in 2M HCl was prepared according to a method based on previous work.[4–6] To a solid of hydrazinium dichloride ($N_2H_4 \cdot 2HCl$) (95 mg, 0.90 mmol) was added a solution of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) (145 mg, 0.60 mmol) in 10 M HCl (10 mL). The mixture was stirred at 80 °C for 3 h and then evaporated in vacuo at 40–50 °C, giving a dark-green residue. The thus-obtained residue was dissolved in a small amount of 10 M HCl and filtered. The filtrate was diluted 100 times with deionized water and transferred to a Dowex 50WX8-100 cation exchange column (12 cm height, 1.8 cm diameter). A brown band consisting of $Mo_2O_4{}^{2+}$ was retained on the column, washed with 0.2 M HCl, and then eluted with 2 M HCl.

The target complex **2** was prepared by the following procedure. To a solution of tropolone (**1**) (37 mg, 0.30 mmol) in ethanol (10 mL) was added the above solution of $Mo_2O_4{}^{2+}$ in 2 M HCl (80 mL). The mixture was stirred at 25 °C for 15 min, resulting in the precipitation of a dark reddish-brown solid. The thus-obtained crude product was carefully washed with ethanol and recrystallized from ethanol to provide the pure complex, $[Mo_2O_4(trop)_2(EtOH)_2]$, with a two molar amount of ethanol as a crystal solvent (63 mg, 92 µmol, 61% yield). The molecular structure was established on the basis of elemental analysis,[7a] spectroscopic data [IR and ^1H and ^{13}C NMR including 2D NMR (i.e., H–H COSY and HMQC)],[7a] and X-ray crystallographic analysis.[7b]

Complex **2**[7a] was dark reddish-brown blocks, mp > 330 °C [decomp., determined by thermal analysis (TGA and DTA)]. An elemental analysis confirmed the molecular formula $C_{14}H_{10}Mo_2O_8$ (Found: C, 33.71; H, 1.96%. Calcd for $C_{14}H_{10}Mo_2O_8$: C, 33.76; H, 2.02%.). The IR (KBr) spectrum showed a specific band based on the stretching of the Mo=O bond at 945 cm^{-1}, which was a low value in comparison with those of **3** (963 cm^{-1}) and **4** (960 cm^{-1}), and two specific bands based on the oscillations of the $[Mo(\mu\text{-}O)_2Mo]$ fragment at 721 and 737 cm^{-1}, which coincided with those of **3** (719 cm^{-1}) and **4** (736 cm^{-1}). The stretching frequencies at 1593 and 1524 cm^{-1}, which showed low values in comparison with those of **1**,[8] were attributed to the coordinated C=O groups and to the C=C bonds with a delocalized π-electron system. The ^1H NMR (DMSO-d_6, 24 °C) spectrum showed signals indicating the two tropolonato ligands are equivalent at $\delta = 7.39$ (2H, brd dd, $J = 9.6$, 9.6 Hz, H-4,4′), 7.47 (4H, brd d, $J = 10.6$ Hz, H-2,2′,6,6′), and 7.80 (4H, brd dd, $J = 10.6$, 9.6 Hz, H-3,3′,5,5′). The ^{13}C NMR (DMSO-d_6, 24 °C) spectrum exhibited the following four carbon signals: $\delta =$ 179.2 (C-1,1′,7,7′), 140.7 (C-3,3′,5,5′), 130.0 (C-4,4′), and 126.6 (C-2,2′,6,6′). The chemical shifts (δ, ppm) for the proton and carbon signals of **2** showed larger down-field shifts, respectively, in comparison with those of **1**.[8]

The crystal structure of **2** with two molecules of ethanol as ligands, $[Mo_2O_4(trop)_2(EtOH)_2]$,[7b] was determined by means of X-ray diffraction, producing accurate structural parameters.[9] The ORTEP drawing of the complex, indicating the molecular structure of di-μ-oxo-bis[(ethanol)oxo(tropolonato)molybdenum(V)], is shown in Fig. 1(a). As a result, the following eight points were found: (i) although the crystal structures of **3** and **4**, respectively, had a crystallographically twofold symmetry axis, the crystal structure of $[Mo_2O_4(trop)_2(EtOH)_2]$ did not have such a crystallographically twofold symmetry axis, (ii) the presence of the structural core, $[O{=}Mo(\mu\text{-}O)_2Mo{=}O]^{2+}$, which formed the *syn* configuration, was observed. This configuration was the same as those of **3** and **4**, (iii) the Mo–Mo

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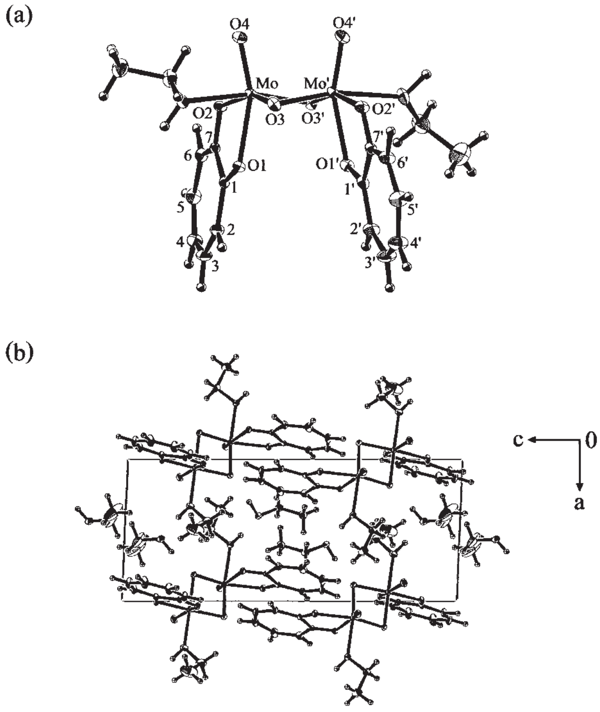

Fig. 1. (a): The ORTEP drawing of $[Mo_2O_4(trop)_2(EtOH)_2]$ with the numbering scheme (30% probability thermal ellipsoids). The solvent molecule (ethanol) is omitted. (b): The packing structure of $[Mo_2O_4(trop)_2(EtOH)_2]$ with a two molar amount of ethanol as a crystal solvent.

distance of 2.5640(2) Å observed for the $[Mo^V{}_2(\mu\text{-}O)_2]$ centers was slightly longer than the Mo–Mo distances observed for **3** [2.549(1) Å] and **4** [2.556(1) Å], (iv) the $[Mo^V{}_2(\mu\text{-}O)_2]$ fragment was not squareplanar as shown in Fig. 1(a) and, further, the Mo–O3, Mo–O3′, Mo′–O3, and Mo′–O3′ bond distances were 1.939(2), 1.945(2), 1.934(2), and 1.947(2) Å, respectively. The two bridging Mo–O bond distances were 1.925(2) and 1.931(2) Å in **3** and 1.923(3) and 1.948(2) Å in **4**, (v) the Mo=O4 and Mo′=O4′ bond distances of the $[O{=}Mo(\mu\text{-}O)_2Mo{=}O]^{2+}$ core were 1.685(2) and 1.687(2) Å, which are the usual values for molybdenum to terminal oxygen bond distances. The Mo=O bond distances of **3** and **4** were 1.678(2) and 1.691(2) Å, respectively, (vi) from a comparative study of the bond angles (°), the coordination geometry for each molybdenum atom of the $[O{=}Mo(\mu\text{-}O)_2Mo{=}O]^{2+}$ centers was more a distorted octahedral with the coordinated tropolonato and ethanol ligands, in comparison with the cases of **3** and **4**, (vii) although clear bond alternation between the single and double bonds for the seven-membered ring of each tropolonato ligand was not observed, suggesting the formation of a delocalized π-electron system, in comparison with the case of tropolone (**1**),[10] the average C–C bond distance for the seven-membered ring of each tropolonato ligand [the left ring: 1.399 Å and the right ring: 1.397 Å in Fig. 1(a)] coincided with the bond distance observed for that of **1** (1.395 Å), and (viii) although the C1–O1, C7–O2, C1′–O1′, and C7′–O2′ bond distances were within a close range of their average bond distance (1.292 Å), the Mo–O1 and Mo′–O1′ bond distances [2.168(2) and 2.160(2) Å] were characteristically longer than the Mo–O2 and Mo′–O2′ bond distances [2.108(1) and 2.102(2) Å]. Moreover, the packing structure of $[Mo_2O_4(trop)_2(EtOH)_2]$ with a two molar amount of ethanol as a crystal solvent revealed that these molecules formed a unique accumulation in the single crystal, as shown in Fig. 1(b).

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7 a) The sample dried well in a vacuum desiccator (at 5×10^{-3} mbar, for 7 days) was rapidly used for thermal, elemental, and spectroscopic analyses. b) The freshly recrystallized sample, which was not dried in a vacuum desiccator, was used for X-ray crystallographic analysis.

8 **1**: IR ν_{max} (KBr) cm^{-1}, 1612 (C=O) and 1551 (C=C); ^{1}H NMR (DMSO-d_6, 24 °C) δ 7.04 (1H, ddd, $J = 9.7$, 9.7, 0.9 Hz, H-4), 7.21, 7.22 (1H each, dd, $J = 10.6$, 0.9 Hz, H-2,6), 7.409, 7.413 (1H each, ddd, $J = 10.6$, 9.7, 0.9 Hz, H-3,5), and 10.13 (1H, brd s, OH); ^{13}C NMR (DMSO-d_6, 24 °C) δ 171.9 (C-1,7), 137.4 (C-3,5), 128.1 (C-4), and 124.6 (C-2,6).

9 Crystallographic data for $[Mo_2O_4(trop)_2(EtOH)_2]\cdot 2EtOH$: $C_{22}H_{34}O_{12}Mo_2$ [FW = 682.38, dark reddish-brown block (the crystal size, $0.20 \times 0.20 \times 0.30$ mm)], triclinic, $P\bar{1}$ (#2), $a = 7.7177(3)$ Å, $b = 9.930(1)$ Å, $c = 18.424(2)$ Å, $\alpha = 80.403(3)°$, $\beta = 86.849(1)°$, $\gamma = 84.035(1)°$, $V = 1383.6(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.638$ g/cm^3, μ (Mo Kα) = 9.62 cm^{-1}, measured reflections = 5835, observed reflections = 5834, $R1 = 0.027$, $wR2 = 0.088$, Goodness of Fit Indicator = 1.82. The X-ray measurement of this complex was made with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) on a Quantum CCD area detector coupled with a Rigaku AFC-7 diffractometer at 200 K. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. 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 number CCDC 220137.

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