Synthesis, Structure and Properties of Tetranuclear Molybdenum(I) Carbonyl Thiolate Complex with Dicarboxylate Bridging Ligand

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A novel complex, $[Bu_4N]_2[\{Mo_2(\mu\text{-}SPh)_2(CO)_6\}_2(\eta^2\text{-}\mu\text{-}O_2C(CH_2)_2CO_2\text{-}\mu\text{-}\eta^2)]$ **1**, is synthesized by the reaction of $[Bu_4N][Mo_2(\mu\text{-}SPh)_2(\mu\text{-}Br)(CO)_6]$ and butanedioic in the present of Et_3N in acetone. X-ray crystal structure of **1** is determined. **1** might possess an electrochemistry character of four-electron reduction in a single step.

Low valence molybdenum carbonyl thiolate compounds have attracted our attention. Of particular interest is the fact that the compounds formulated as $Mo_2(\mu\text{-}SR)_2(CO)_8$ (R = Ph,[1, 2] CH_2CO_2Et[3]), $Mo_2(\mu\text{-}SR)_2(CO)_6(MeCN)_2$,[4] undergo electrochemically reversible two-electron transfer in a single step. In this communication, we describe the synthesis, crystal structure, and some spectra and electrochemistry properties of the first tetranuclear molybdenum(I) complex **1**.

Excess Et_3N was added at mild temperature to a suspension of butanedioic(60 mg, 0.5 mmol) in dried, degassed acetone under nitrogen affording a colorless solution, then a solid of $[Bu_4N][Mo_2(\mu\text{-}SPh)_2(\mu\text{-}Br)(CO)_6]$ (900 mg, 1 mmol) (prepared by the reaction of $Mo_2(\mu\text{-}SR)_2(CO)_8$ and Bu_4NBr) was added, and the resulting mixture was stirred at moderate temperature for several hours, the color of reaction solution turn green from brown during this time. After a continuous stirring at room temperature overnight, the resulting green solution was filtered to remove Et_3NHBr and taken to dryness to remove Et_3N, the resulting solid was dissolved in 10 ml acetone, subsequent added i-PrOH (20 ml). This mixture was allowed to stand below 0 °C for a few days, X-ray quality crystals formed. These were collected with filtration, washed with a small amount of i-PrOH and dried in vacuo (yield 600 mg, 68%).[5] The structure of $[Bu_4N]_2[\{Mo_2(\mu\text{-}SPh)_2(CO)_6\}_2(\eta^2\text{-}\mu\text{-}O_2C(CH_2)_2CO_2\text{-}\mu\text{-}\eta^2)]$ **1**, has been also determined.[6]

A perspective drawing of the complex dianion of **1** with atomic numbering is shown in Figure 1. Each Mo(I) atom is located in a distorted octahedral environment with three carbon atoms from carbonyl, two bridging sulfur atoms from phenylthiolate groups and one oxygen atom from carboxylate group. It can be observed in the dianion of **1** that two planar Mo_2S_2 units with Mo—Mo single bond (2.9193(3) Å) meeting the requirement of 18-electron rule are linked by a butanedioic ligand forming tetranuclear double Mo_2S_2 unit complex, and the phenyl groups of each Mo_2S_2 plane are in an anti configuration, but those of $[Bu_4N][Mo_2(\mu\text{-}SPh)_2(\mu\text{-}Br)(CO)_6]$ are in a syn orientation. The Mo_2S_2 units in **1** are similar to that in $Mo_2(\mu\text{-}SPh)_2(CO)_8$,[7] but it incurs 0.043 Å shorter Mo—Mo distance and 1.00° smaller MoSMo angle than that in $Mo_2(\mu\text{-}SPh)_2(CO)_8$ by introducing the carboxylate bridge ligand into the Mo_2S_2 unit in **1**. The butanedioic ligand has two bridging functions: not only bridges two Mo(I) atoms of each Mo_2S_2 unit, but also links two Mo_2S_2 units of the tetranuclear complex together. The five member ring Mo(1)Mo(2)O(12)C(31)O(11) is a plane with a dihedral angle of 98.11° relative to the Mo_2S_2 plane. It is worth noting that the coordination of the dicarboxylate ligand in **1** was found in the tetranuclear Mo(II) complex $[Mo_4(O_2C(CH_2)_2CO_2)_2(MeCN)_{12}][BF_4]_4$[8] and in the tetranuclear Mo(V) complex $K_6[\{Mo_2O_4(mal)_2\}_2(mal)]\cdot H_2O$.[9] To our knowledge, complex **1** is the first structure for tetranuclear Mo(I). While compared to the above Mo(II) complex and Mo(V) complex, complex **1** has significantly different Mo—Mo, Mo—O distanceas and OMoMo angle. The mean Mo—Mo distance of **1** (2.9193 Å) is 0.767 Å longer than that of the Mo(II) complex (2.1415 Å) and 0.364 Å longer than that of the Mo(V) complex (2.5555 Å). The mean Mo—O distance of complex **1** (2.229 Å) is 0.135 Å longer than that of the Mo(II) complex (2.084 Å) and 0.10 Å shorter than that of the Mo(V) complex (2.321 Å), and the mean OMoMo angle of **1** (81.22°) decreases 9.6° relative to that of the Mo(II) complex (90.85°).

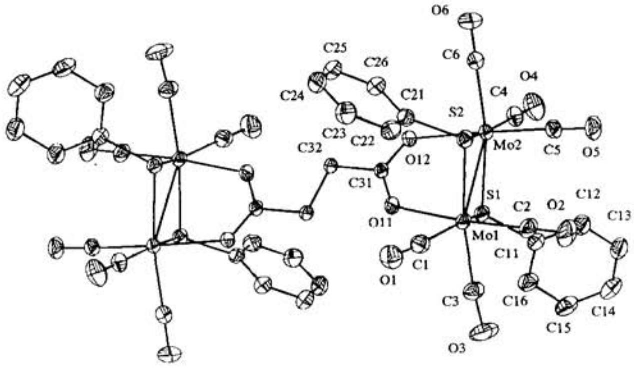

Figure 1. Perspective drawing of the complex dianion of **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Mo(1)-C(2) 1.950(3), Mo(1)-C(3) 1.988(3), Mo(1)-C(1) 2.016(3), Mo(1)-O(11) 2.226(2), Mo(1)-S(1) 2.4323(7), Mo(1)-S(2) 2.4619(7), Mo(1)-Mo(2) 2.9193(3), C(31)-O(11) 1.256(3); S(1)-Mo(1)-S(2) 108.65(2), O(11)-Mo(1)-Mo(2) 80.99(5), Mo(1)-S(1)-Mo(2) 72.98(2), O(11)-C(31)-O(12) 125.8(2).

Because of different trans-effect, the trans Mo—C distances are a little shorter than those cis-ones to butanedioic ligand, thus, the trans CO groups become more difficult to be substituted than cis-CO. This might be the reason why the chain complex, similar to what proposed by M. H. Chisholm,[10] wasn't obtained.

The IR spectrum (KBr pellet) of **1** showed two strong absorption at 1552 and 1413 cm^{-1}, which are obviously the characteristic vibration frequencies of carboxylate $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$. The value of $\Delta\nu$ (OCO) (ν_{asym} - ν_{sym}) as a measure for the coordinating mode of carboxylate group, which of **1** (139 cm^{-1}) is less than that in the free ionic complex ($KO_2C(CH_2)_2CO_2K$, $\Delta\nu = 1570 - 1420 = 150\ cm^{-1}$), indicating the bridging mode of butanedioic in **1**. This is consistent with Deacon and Philips' conclusion.[11] In fact, the structure of **1** also supports this result.

The ^{95}Mo NMR chemical shift for **1** is -726.47 ppm, which is at more down filed than that of $Mo_2(\mu\text{-}SPh)_2(CO)_8$ (-1112.30 ppm) and $[Bu_4N][Mo_2(\mu\text{-}SPh)_2(\mu\text{-}Br)(CO)_6]$ (-747.60 ppm), indicating a larger deshielding for butanedioic than carbonyl ligand and bromine bridge. Only one ^{95}Mo NMR chemical shift being observed in **1** is consistent with the result from structure study that the geometries of the four Mo atoms in **1** are essentially identical.

The cyclic voltammograms[12] of **1** in acetone (Figure 2.) showed an irreversible reduction peak at -1.05 V (*vs* SCE), two irreversible oxidation peaks at -0.95 V and -0.85 V, and a redox couple at *ca* 0.43 V (0.46 V/0.40 V). Compared with ferrocene, which was generally known to undergo a discrete one-electron transfer process, the voltammetric peak current parameter ($i_p/\upsilon^{1/2}AC$) of 2550 $\mu A\ s^{1/2}\ V^{-1/2}\ cm^{-2}\ mM^{-1}$ for the irreversible reduction peak at -1.05 V is nearly the quadruple of that observed for the ferrocene (690 $\mu A\ s^{1/2}\ V^{-1/2}\ cm^{-2}\ mM^{-1}$). It can be considered as four-electron reduction in a single step. According to the two-electron transfer character of $Mo_2(SR)_2(CO)_8$,[1] the four-electron reduction nature of **1** is reasonably attributed to the cleavage of two equivalent metal—metal bonds in the two Mo_2S_2 units, giving an 18-electron configuration around each Mo(0) atom. This is consistent with the fact that only one ^{95}Mo NMR chemical shift was observed in **1** and the geometries of the four Mo atoms in **1** are essentially identical. The couple (1340 $\mu A\ s^{1/2}\ V^{-1/2}\ cm^{-2}\ mM^{-1}$) at *ca* 0.43 V might reflect the electrochemical behavior of the whole complex **1** as Eq. (1).

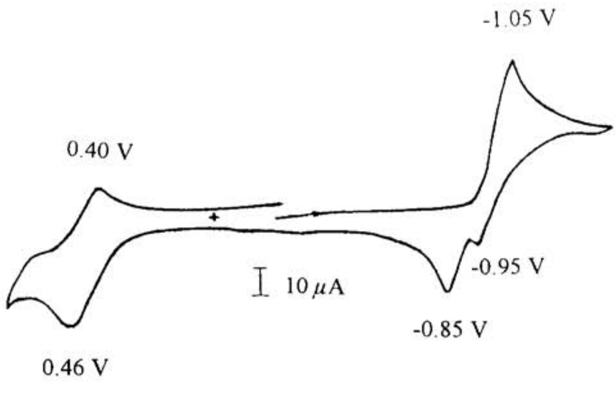

Figure 2. Cyclic voltammograms of **1** in acetone; concentration, 0.0002 M; scan rate, 100 mV/s.

$$[\{Mo_2(SPh)_2(CO)_6\}_2(O_2C(CH_2)_2CO_2)]^{2-} \xrightleftharpoons[2\,e]{0.43\ V} [\{Mo_2(SPh)_2(CO)_6\}_2(O_2C(CH_2)_2CO_2)] \quad (1)$$

the irreversible two oxidation peaks at negative potentials are naturally relative to oxidation of the product derived from four-electron reduction process.

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References and Notes

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5 Selected ^1H NMR(CD_3COCD_3): δ(ppm) 2.1(s 4H CH_2), 7.1-7.5(s 20H Ph); selected IR(KBr) $\nu_{co}(cm^{-1})$: 1990, 1940, 1918, 1855, 1832. UV/vis λ_{max} (nm): 660, 440, 380. Anal. Found: H, 5.56; C, 49.17; N, 1.55%. Calcd. for $C_{72}H_{96}Mo_4N_2O_{16}S_4$: H, 5.51; C, 49.20; N, 1.59%.
6 Crystal data for **1**: $C_{72}H_{96}Mo_4N_2O_{16}S_4$ Mr = 1757.5, triclinic, space group P-1, a = 10.9951(2), b = 12.8830(1), c = 16.2324(3) Å, α = 73.569(1), β = 70.456(1), γ = 69.833(1)°, V = 1997.17(5) $Å^3$, Z = 1, Dc = 1.461 g/cm^3, T = 293(2) K, Siemens Smart CCD diffractometer, ω scan, λ(Mo-kα) = 0.71073 Å, θ = 2.71—30.05°, F(000) = 902. 11321 unique reflections [R(int) = 0.0171] were collected and 9064 reflections with $I=2\sigma(I)$ were used in the structural refinement, R1 = 0.0356, wR2 = 0.0740. All structural analyses and calculations were performed on a Indyworkstation of a silicon Graphics instrument with SHELXTL local program.[13]
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