

Dicyclopentamethylenethiuram Disulfide as Precursor of Mononuclear Complexes: Oxidative Cleavage of Metal-Metal Bond in $[\text{CpMo}(\text{CO})_3]_2$ and Molecular Structure of *cis*- $[\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C-N}(\text{CH}_2)_5\}]$

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Abstract

The reaction of $[\text{CpMo}(\text{CO})_3]_2$ with dicyclopentamethylenethiuram disulfide in refluxing xylene resulted a novel mono nuclear complex, *cis*- $[\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C-N}(\text{CH}_2)_5\}]$ as red crystals in moderate yield. The compound was formed by the oxidative cleavage of metal-metal bond in $[\text{CpMo}(\text{CO})_3]_2$ together with a reductive sulfur-sulfur bond scission in the ligand.

Keywords

Dicyclopentamethylenethiuram Disulfide (Dcpmtd), Oxidation Number, Oxidative Cleavage, Coordination Number, Mononuclear Complex, X-Ray Crystal Structure

1. Introduction

Dithiocarbamate ligands are versatile ligands with applications in industry [1], agriculture [2] and biology [3]. Since these ligands contain nitrogen and sulfur donor atoms, they are capable of forming complexes with most of the elements [4]. A number of dithiocarbamate complexes have been reported in literature [5]-[12] with various geometries such as square planar [13], octahedral [14] [15] and trigonal prismatic [16]. Interestingly, their pyridine [6] [7] [17], 2,2'-bipyridine [7]

[9] triphenylphosphine [18], and 1,10-phenanthroline [9] [17] adducts have been reported to possess similar donor properties. These ligands may stabilize monatomic metal ions in various oxidation states because of its chelating capacity thus forming mononuclear complexes [19]-[28]. The anionic form of N,N-dialkyl-1,1-dithio-ligands is stable and the stability stems from the resonance of the anionic form of the ligand (**Figure 1**) [19].

Shi *et al.* reported the reaction between $[\text{CpMo}(\text{CO})_2]_2$ with tetramethylthiuram disulfide which yielded the mononuclear cyclopentadienyl molybdenum dithiocarbamate complex *cis*- $[(\text{CpMo}(\text{CO})_2)_2\{\text{S}_2\text{C-N}(\text{CH}_3)_2\}]$ [29]. The compound is formed by oxidative cleavage of Mo-Mo triple bond together with a reductive S-S bond scission in tetramethylthiuram disulfide ligand (**Scheme 1**).

2. Results

We carried out the analogous reaction of dicyclopentamethylenethiuram disulfide with $[\text{CpMo}(\text{CO})_3]_2$ and reported herein the formation of a mononuclear cyclopentadienyl molybdenum dicarbonyl complex, *cis*- $[(\text{CpMo}(\text{CO})_2)_2\{\text{S}_2\text{C-N}(\text{CH}_2)_5\}]$.

Treatment of $[\text{CpMo}(\text{CO})_3]_2$ with dicyclopentamethylenethiuram disulfide in refluxing xylene gave thermally stable complex *cis*- $[(\text{CpMo}(\text{CO})_2)_2\{\text{S}_2\text{C-N}(\text{CH}_2)_5\}]$ as major reaction product (**Scheme 2**) which has been characterized by elemental analysis and spectroscopic methods [30]. The structure of the complex has been determined by single crystal X-ray diffraction [31] which is summarized in **Figure 2**.

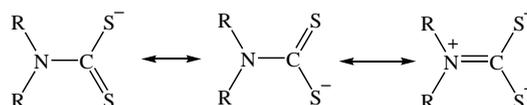


Figure 1. Resonance structures of anionic N,N-dialkyl-1,1-dithio ligand.

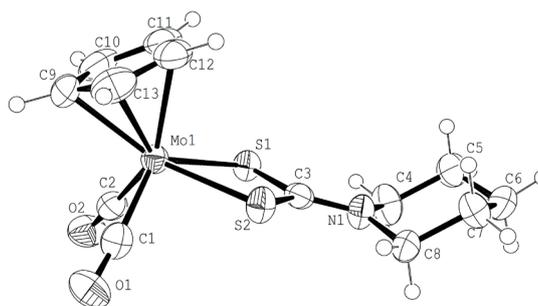
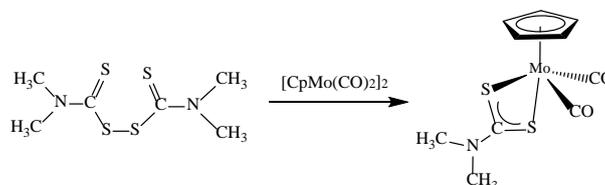
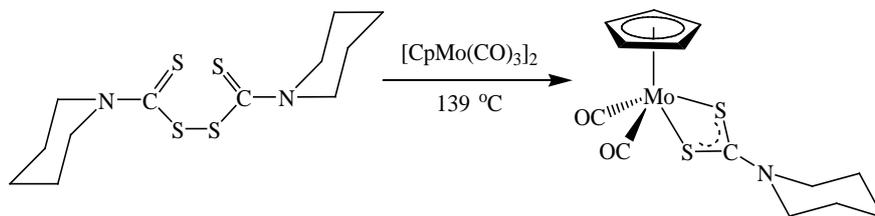


Figure 2. Molecular structure of *cis*- $[(\text{CpMo}(\text{CO})_2)_2\{\text{S}_2\text{C-N}(\text{CH}_2)_5\}]$.



Scheme 1. Oxidative cleavage of Mo-Mo triple bond in thiuram disulfide by $[\text{CpMo}(\text{CO})_2]_2$.



Scheme 2. Synthesis of *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}].

The molecular structure of *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] shows a four-legged piano-stool configuration at Mo(II), being coordinated to a bidentate cyclopentamethylene dithiocarbamate and two CO ligands, similar to the coordination found in the analogous complex ion *cis*-[(CpMo(CO)₂{S₂C-N(CH₃)₂}] (**Scheme 2**) [29]. Bond lengths S(1)-C(3) and S(2)-C(3) have been found 1.708(5) Å, which is consistent with the partial C-S double bond [32]. The average Mo-C(Cp) bond distance in *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] has been found to be 2.326 Å, which is similar to the Mo-C(Cp) average bond distance of 2.325 Å as found in *cis*-[(CpMo(CO)₂{S₂C-N(CH₃)₂}] [29]. Mo-S bond distance in *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] was found 2.500 Å which is similar to the average Mo-S bond distance reported in *cis*-[(CpMo(CO)₂{S₂C-N(CH₃)₂}] (2.503 Å) [29]. Average Mo-CO bond distance in *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] is 1.962 Å. Similar average Mo-CO bond distance 1.958 Å was found in *cis*-[(CpMo(CO)₂{S₂C-N(CH₃)₂}] (**Figure 2**) [29].

Selected bond lengths [Å] and bond angles [°]: Mo(1)-C(1) 1.958(6), Mo(1)-C(2) 1.966(6), Mo(1)-C(9) 2.275(6), Mo(1)-C(10) 2.300(6), Mo(1)-C(13) 2.306(6), Mo(1)-C(12) 2.363(6), Mo(1)-C(11) 2.384(6), Mo(1)-S(1) 2.505(2), Mo(1)-S(2) 2.495(3), S(1)-C(3) 1.708(5), S(2)-C(3) 1.708(5), C(2)-Mo(1)-C(1) 5.7(2), C(2)-Mo(1)-S(1) 81.47(19), C(1)-Mo(1)-S(1) 121.98(18), S(2)-Mo(1)-S(1) 68.55(7).

The complex, *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] was obtained by the oxidative cleavage of the Mo-Mo bond in [CpMo(CO)₃]₂ which is consistent with the increase in oxidation number of Mo atom in the complex from +1 to +2. The geometry of the compound can be described as square-pyramidal with Cp-Mo defining the vertex and C(1), C(2), S(1) and S(2) atoms defining the base. The base of this complex is not a regular square because of unequal bond lengths of Mo-S and Mo-C bonds. In complex *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}], the cyclopentadienyl ligand acts as five electron donor and dithiocarbamate acts as three electron donor ligand. The complex is thermally stable and follows 18-electron rule.

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- [30] To a xylene (40 mL) of [CpMo(CO)₃]₂ (0.200 g, 0.408 mmol) Was Added Dicyclopentamethylenethiuram Disulfide (0.196 g, 0.612mmol) and the Reaction Mixture Was Refluxed for 1 Hour. The Color Was Changed from Red to Red Brown. The Solvent Was Removed under Reduced Pressure and Residue Chromatographed by TLC on Silica. Elution with Cyclohexane/Dichloromethane (3:2 V/V) Gave One Band *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] (0.167 g, 36.16%) as Red Brown Crystal from Dichloromethane/Hexane Mixture at -4 °C. Elemental Analysis: Found C = 41.36, H = 3.99, N = 3.70, S = 16.94% and C₁₃H₁₅MoNO₂S₂ Requires C = 41.34, H = 3.98, N = 3.71, S = 16.96%. IR (ν_{CO}) in cm⁻¹: 1857.53(s), 1949.15(s). ¹H NMR (ppm): 1.54 (m, 3H), 1.63 (m, 3H), 3.56 (m, 2H), 3.79 (m, 2H), 5.41 (s, 5H). FAB mass (m/z):377 [M⁺], 349 [M⁺-CO], 321 [M⁺-2CO], 257 [M⁺-2CO-2S], etc.
- [31] Crystal Data for *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] : Empirical Formula C₁₃H₁₅MoNO₂S₂, MW = 377.32, Triclinic, Space groupP1, a = 6.449(7) Å, b = 10.634(10) Å, c = 11.383(12) Å, α = 71.94(3)°, β = 82.31(3)°, γ = 76.43(3)°, V = 719.9(13) Å³, T = 273(2) K, Z = 2, μ = 1.197 mm⁻¹, F(000) 380, density (calculated) 1.741 Mg/m³, 7722 Reflections Collected, 3303 Independentreflections [R(int) = 0.0477]. The Final R1 = 0.0486, wR2 = 0.1288 [I > 2 σ (I)], R Indices (all data) R1 = 0.0719, wR2 = 0.1566.
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Supplementary Material

Crystallographic data for *cis*-[(CpMo(CO)₂{S₂C-N(CH₂)₅}] has been deposited at the Cambridge Crystallographic Centre with CCDC Reference Number CCDC 1567351. Copy of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Tel: +441223 336408; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk)).