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

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Abstract

The reaction of \([\text{CpMo(CO)}_3]_2\) with dicyclopentamethylenethiuram disulfide in refluxing xylene resulted a novel mono nuclear complex, \(\text{cis-}[\text{CpMo(CO)}_2\{\text{S}_2\text{C-N(CH}_2\text{)}_5\}]\) as red crystals in moderate yield. The compound was formed by the oxidative cleavage of metal-metal bond in \([\text{CpMo(CO)}_3]_2\) 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 [CpMo(CO)2]2 with tetramethylthiuram disulfide which yielded the mononuclear cyclopentadienyl molybdenum dithiocarbamate complex cis-[(CpMo(CO)2[S2C-N(CH3)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 [CpMo(CO)3]2 and reported herein the formation of a mononuclear cyclopentadienyl molybdenum dicarbonyl complex, cis-[(CpMo(CO)2[S2C-N(CH2)5]].

Treatment of [CpMo(CO)3]2 with dicyclopentamethylenethiuram disulfide in refluxing xylene gave thermally stable complex cis-[(CpMo(CO)2[S2C-N(CH2)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.

![Image](image1.png)

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

![Image](image2.png)

Figure 2. Molecular structure of cis-[(CpMo(CO)2[S2C-N(CH2)5]].

![Image](image3.png)

Scheme 2. Synthesis of cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_2)_5)]\).

The molecular structure of cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_2)_5)]\) 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-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) (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-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) 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-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) \[29\]. Mo-S bond distance in cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) was found 2.500 Å which is similar to the average Mo-S bond distance reported in cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) (2.503 Å) \[29\]. Average Mo-CO bond distance in cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) is 1.962 Å. Similar average Mo-CO bond distance 1.958 Å was found in cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) (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) 2.306(6), Mo(1)-C(10) 2.300(6), Mo(1)-C(12) 2.306(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) 68.55(7). The complex, cis-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\) was obtained by the oxidative cleavage of the Mo-Mo bond in \([\text{Cp} \text{Mo}(\text{CO})_3]_2\) which is consistent with the increase in oxidation number of the 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-\([(\text{Cp} \text{Mo} (\text{CO})_2 S_2 \text{C} - \text{N} (\text{CH}_3)_2)]\), 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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References


[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 (υ=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 =273(2) K, Z= 2, μ=1.197 mm⁻¹, F(000) 380, density (calculated) 1.741 Mg/m³, 7722 Reflections Collected, 3303 Independent reflections [R(int) = 0.0477]. The Final R1 = 0.0486, wR2 = 0.1288 [I > 2σ (I)], R Indices (all data) R1 = 0.0719, wR2 = 0.1566.


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: +44 1223 336408; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk)).