

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*- $[\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_2)_5\}]$

Md. Manzurul Karim^{1*}, Shafikul Islam², Md. Rafikul Islam³, Mohammad R. Karim^{4*},
Tasneem A. Siddiquee⁴

¹Department of Chemistry, Jahangirnagar University, Savar, Bangladesh

²Department of Chemistry, Morning Glory School and College, Savar, Bangladesh

³Department of Chemistry, Barisal Cadet College, Barisal, Bangladesh

⁴Department of Chemistry, Tennessee State University, Nashville, TN, USA

Email: *karim_ju1958@yahoo.com, chem.shafik@gmail.com, rafikchemju@gmail.com, *mkarim@tnstate.edu

How to cite this paper: Karim, M.M., Islam, S., Rafikul, I.M., Karim, M.R. and Siddiquee, T.A. (2017) 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*- $[\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_2)_5\}]$. *Crystal Structure Theory and Applications*, 6, 67-72.

<https://doi.org/10.4236/csta.2017.64006>

Received: October 18, 2017

Accepted: November 27, 2017

Published: November 30, 2017

Copyright © 2017 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The reaction of $[\text{CpMo}(\text{CO})_3]_2$ with dicyclopentamethylenethiuram disulfide in refluxing xylene resulted a novel mono nuclear complex, *cis*- $[\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_2)_5\}]$ 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*- $[(\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_3)_2\})]$ [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*- $[(\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_2)_5\})]$.

Treatment of $[\text{CpMo}(\text{CO})_3]_2$ with dicyclopentamethylenethiuram disulfide in refluxing xylene gave thermally stable complex *cis*- $[(\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_2)_5\})]$ 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**.

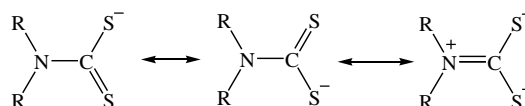


Figure 1. Resonance structures of anionic N,N-dialkyl-1,1-dithio ligand.

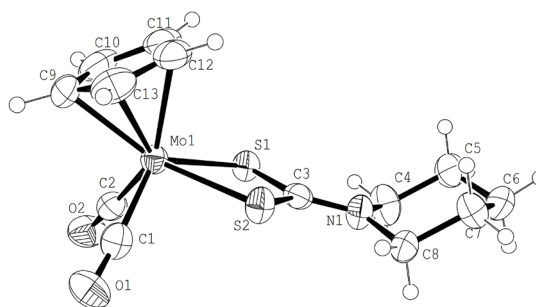
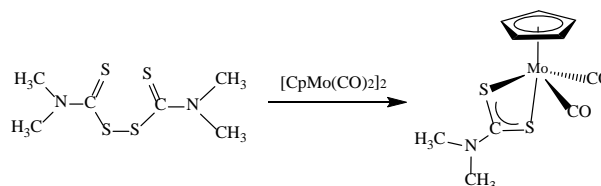
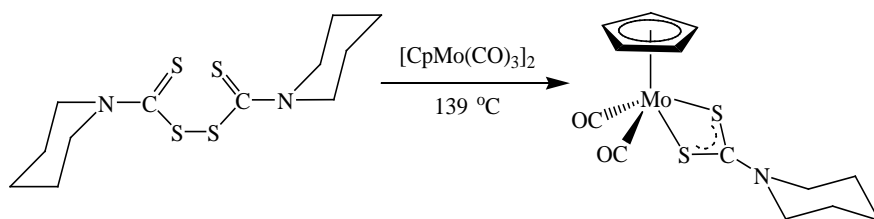


Figure 2. Molecular structure of *cis*- $[(\text{CpMo}(\text{CO})_2\{\text{S}_2\text{C}-\text{N}(\text{CH}_2)_5\})]$.



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}]₂.

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.

Acknowledgements

The authors acknowledge ministry of science and technology, Bangladesh for financial assistance and Department of chemistry, Jahangirnagar University for providing the laboratory facility.

References

- [1] Amdio, E., Cavinato, G., Domella, A., Ronchini, L., Toniolo, L. and Vavasori, A. (2009) New Carboalkoxybis(Triphenylphosphine)Palladium(II) Cationic Complexes: Synthesis, Characterization, Reactivity and Role in the Catalytic Hydrocarboalkoxylation of Ethene. X-Ray Structure of Trans-[Pd(COOMe)(TsO)(PPh₃)₂].2CHCl₃. *Journal of Molecular Catalysis A: Chemical*, **298**, 103.
<https://doi.org/10.1016/j.molcata.2008.10.002>
- [2] European Food Safety Authority (EFSA) (2011) The European Union Report on Pesticide Residues. *EFSA*, **9**, 2430.
- [3] Rehman, M., Hussain, A., Rehman, Z., Rauf, F.A., Hassan, A., Tahir, A. and Ali, S. (2010) New Tetrahedral, Square-Pyramidal, Trigonal-Bipyramidal and Octahedral Organotin(IV) 4-Ethoxycarbonylpiperazine-1-Carbodithioates: Synthesis, Structural Properties and Biological Applications. *Journal of Organometallic Chemistry*, **695**, 1526. <https://doi.org/10.1016/j.jorganchem.2010.03.008>
- [4] Brown Jr., T.L., Lemayand, E.H. and Bursten, B.E. (2000) Chemistry: The Central Science. 8th Edition, Prentice Hall International, Washington.
- [5] Doadrio, A.L., Sotelo, J. and Fern'andez-Ruano, A. (2002) Synthesis and Characterization of Oxovanadium(IV) Dithiocarbamates with Pyridine. *Quimica Nova*, **25**, 525. <https://doi.org/10.1590/S0100-40422002000400002>
- [6] Sharma, M. and Sachar, R. (2009) Synthesis and Characterization of the Adducts of bis(N,N-Diethyldithiocarbamato)Oxovanadium(IV) with Substituted Pyridines. *Oriental Journal of Chemistry*, **25**, 215.
- [7] Manohar, A., Ramalingam, K., Bocelli, G. and Cantoni, A. (2010) Synthesis, Spectral and Single Crystal X-Ray Structural Studies on bis(2,2'-bipyridine)Sulphidom(II) (M = Cu or Zn) and Diaqua 2,2'-Bipyridine Zinc(II)Sulphatedihydrate. *Journal of the Serbian Chemical Society*, **75**, 1085. <https://doi.org/10.2298/JSC091019097M>
- [8] Ekennia, A.C. (2013) Antibacterial Application of Novel Mixed-Ligand Dithiocarbamate Complexes of Nickel (II). *Journal of Applied Chemistry*, **5**, 36.
- [9] Geetha, N. and Thirumaran, S. (2008) Characterization Studies and Cyclic Voltammetry on Nickel(II) Amino Acid Dithiocarbamates with Triphenylphosphine in the Coordination Sphere. *Journal of the Serbian Chemical Society*, **73**, 169.
<https://doi.org/10.2298/JSC0802169G>
- [10] Sovilj, S.P., Vuckovic, G., Leovac, M. and Minic, D. (2000) Dinuclear Copper(II) Complexes of N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane and Some N,S or N,O Bidentate Ligands. *Polish Journal of Chemistry*, **74**, 945.
- [11] Sharma, M., Sharma, A. and Sachar, R. (2013) Preparation and Characterization of the Adducts of bis(N,N-diethyldithiocarbamato)oxovanadium(IV) and copper(II) with n-propylamine and Isopropylamine. *Chemical Science Transactions*, **2**, 367.
<https://doi.org/10.7598/cst2013.265>
- [12] Sharma, M., Sharma, A. and Sachar, R. (2012) Synthesis and Characterization of the Adducts of Morpholinedithiocarbamate Complexes of Oxovanadium(IV), Nickel(II) and Copper(II) with Piperidine and Morpholine. *Journal of Chemistry*, **9**, 1929. <https://doi.org/10.1155/2012/689501>
- [13] Onwudiwe, D.C. and Ajibade, P.A. (2011) Synthesis, Characterization and Thermal Studies of Zn(II), Cd(II) and Hg(II) Complexes of N-methyl-N-phenyl Dithiocarbamate: The Single Crystal Structure of [(C(6)H(5))(CH(3))NCS(2)](4)Hg(2). *International Journal of Molecular Sciences*, **12**, 1964.
<https://doi.org/10.3390/ijms12031964>

- [14] Osowole, A.A., Kolawole, G.A. and Fagade, O.E. (2005) Synthesis, Physicochemical, and Biological Properties of Nickel(II), Copper(II), and Zinc(II) Complexes of an Unsymmetrical Tetradentate Schiff Base and Their Adducts. *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry*, **35**, 829. <https://doi.org/10.1080/15533170500358168>
- [15] Kolawole, G.A. and Osowole, A.A. (2009) Synthesis and Characterization of Some metal(II) Complexes of Isomeric Unsymmetrical Schiff Bases and Their Adducts with Triphenylphosphine. *Journal of Coordination Chemistry*, **62**, 1437. <https://doi.org/10.1080/00958970802621512>
- [16] Guo, T., Lai, C.S., Tan, X.J., Teo, C.S. and Tiekink, E.R. (2002) Bis(diethyldithiocarbamate) (4,7-dimethyl-1,10-phenanthroline)cadmium(II) Acetonitrile Solvate. *Acta Crystallographica-Section E: Structure Reports Online*, **58**, 439. <https://doi.org/10.1107/S1600536802012679>
- [17] Shashi, B.K., Geetanji, K. and Priyanka (2011) Synthesis and Characterization of Pyridine Adducts of Some Transition Metal 4-Methylpiperazine-1-Carbodithioic Acid Complexes. *Himachal Pradesh University Journal*, **1**.
- [18] Mamba, S.M. (2011) Synthesis, Characterization and Application of Dithiocarbamate Transition Metal Complexes. PhD Thesis, University of Johannesburg, Johannesburg.
- [19] Karlin, K.D. (2005) Progress in Inorganic Chemistry. John Wiley and Sons, Inc., 53, 71.
- [20] Deeming, A.J., Forth, C. and Hogarth, G. (2007) Synthesis and Crystal Structure of $[\text{Ru}_8(\mu_5\text{-S})_2(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-CNMe}_2)_2(\mu\text{-CO})(\text{CO})_{15}]$ Formed via the Double Sulphur-Carbon Bond Cleavage of dithiocarbamate ligands. *Journal of Organometallic Chemistry*, **692**, 4000. <https://doi.org/10.1016/j.jorganchem.2007.05.044>
- [21] Karim, M.M., Abser, M.N., Hassan, M.R., Ghosh, N., Alt, H.G., Richards, I. and Hogarth, G. (2012) Oxidative-Addition of Thiuram Disulfides to Osmium(0): Synthesis of cis- $[\text{Os}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2]$ (R = Me, Et, Cy, $\text{CH}_2\text{CH}_2\text{OMe}$) and Molecular Structures of cis- $[\text{Os}(\text{CO})_2(\text{S}_2\text{CNMe}_2)_2]$ and $[(\text{MeOCH}_2\text{CH}_2)_2\text{NCS}]_2$. *Polyhedron*, **42**, 84. <https://doi.org/10.1016/j.poly.2012.04.042>
- [22] Ziegler, M.L., Weber, H., Nuber, B. and Serhadle, O. (1987) Synthesis and Characterization of the Zwitterion $\text{S}_2\text{CC}(\text{NMe}_2)_2$, a Transition Metal Induced Carbon-Carbon Coupling. Complex Chemistry of the Zwitterions $\text{S}_2\text{CC}(\text{NR}_2)_2$. *Zeitschrift für Naturforschung*, **42b**, 141.
- [23] Catheline, D., Roman, E. and Astruc, D. (1984) Reactivity of the Monodentate dithiocarbamate Ligand in $\text{CpFe}(\text{CO})_2(\eta^1\text{-S}_2\text{CNR}_2)$. *Inorganic Chemistry*, **23**, 4508. <https://doi.org/10.1021/ic00194a021>
- [24] Maheu, L.J., Miessler, G.L., Berry, J., Burow, M. and Pignolet, L.H. (1983) Di- and Tri-thiocarbamate Complexes of Osmium(III) and the Crystal and Molecular Structure of $[\text{Os}_2(\text{SeS}_2\text{CNMe}_2)_2(\text{S}_2\text{CNMe}_2)_3]\text{PF}_6$. *Inorganic Chemistry*, **22**, 405. <https://doi.org/10.1021/ic00145a009>
- [25] Hope, J.M., Martin, R.L., Taylor, D. and White, A.H. (1977) Ring Expansion in a Metal-Dithiocarbamate Complex by Oxygen Insertion; Synthesis and Properties of $[\text{Cr}(\text{S}_2\text{CNR}_2)_2(\text{OS}_2\text{CNR}_2)]$. The X-Ray Structure of bis[NN-diethyl (dithiocarbamate-SS')][NN-diethyl(dithioperoxycarbamate-OS)]chromium(III). *Journal of the Chemical Society, Chemical Communications*, 99. <https://doi.org/10.1039/C39770000099>
- [26] Martin, R.L., Patrick, J.M., Skelton, B.W., Taylor, D. and White, A.H. (1982) Crystal Structure of bis[N,N-diethyl(dithiocarbamate-S,S')]-[N,N-diethyl (dithioperoxycarbamate-O,S)]chromium(III). A Redetermination. *Australian Journal of Chemi-*

- stry, **35**, 2551. <https://doi.org/10.1071/CH9822551>
- [27] Fackler, J.P. and Holah, D.G. (1966) Sulfur Chelates. II. Five-Coordinate Transition Metal Complexes. *Inorganic and Nuclear Chemistry Letters*, **2**, 251. [https://doi.org/10.1016/0020-1650\(66\)80055-7](https://doi.org/10.1016/0020-1650(66)80055-7)
- [28] Pignolet, L.H., Lewis, R.A. and Holm, R.H. (1971) Synthesis and Stereochemical Rearrangements of Complexes Containing the Fe-S6 Core. *Journal of the American Chemical Society*, **93**, 360. <https://doi.org/10.1021/ja00731a011>
- [29] Shi, Y., Cheng, G., Lu, S., Guo, H., Wu, Q., Huang, X. and Hu, N. (1993) The Cleavage Reaction of the Molybdenum-Molybdenum Triple Bond. The Crystal Structures of Molybdenum Complexes [CpMo(CO)2(C5H4NS)], [CpMo(CO)2(C9H6NS)]O:PPh3 and [CpMo(CO)2(S2CNMe2)]. *Journal of Organometallic Chemistry*, **455**, 115. [https://doi.org/10.1016/0022-328X\(93\)80389-S](https://doi.org/10.1016/0022-328X(93)80389-S)
- [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 group P1, 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 Independent reflections [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.
- [32] Lide, D.R. (2003-2004) Handbook of Chemistry and Physics. 84th Edition, CRC Press, Sec. 9, 10.

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)).