Synthesis, Spectroscopic and Quantum Chemical Studies of a Novel Cis-dioxomolybdenum(vi) Thiosemicarbazonate Complex

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Abstract—The synthesis and characterization of dioxomolybdenum(VI) chelate complexes with 5-chloro-4methyl-2-hydroxybenzophenone S-methyl-4phenylthiosemicarbazone (L) in the form of [MoO₂(L)D] where D is the nitrogen donor ligand, namely pyridine in this complex system. The mixed-ligand complexes were characterized by using elemental analysis, UV-Vis, Mid-IR and ¹H-NMR spectroscopic techniques. In addition, optimized geometries and vibrational wavenumbers of the complexes were calculated DFT/B3LYP functional with LANL2DZ basis set. The assignment of the vibrational modes was performed based on the total energy distribution (TED).

Index Terms—Benzophenone, thiosemicarbazone, dioxomolybdenum(VI), vibrational spectra, TED, NBO.

I. INTRODUCTION

Thiosemicarbazones are an important class of compounds with beneficial biological activity; they have been shown to have antitumor, antiviral, antitubercular, antibacterial, antihypertensive and antimalarial activities.

Molybdenum thiosemicarbazone complexes have attracted much interest due to their unique advantages in forming compound type MoO₂L which possess one "open" coordination sites that can be utilized for substrate binding [1], [2]. Therefore, the mononuclear dioxomolybdenum complexes might be interesting model systems. In recent years, a number of dioxomolybdenum complexes have been synthesized and characterized to mimic the biological systems [3]. There is almost universal agreement in the literature that for both the free ligands and metal complexes dialkylation of the terminal nitrogen increases in vitro cytotoxicity and that activity decreases with increasing lipophilicity of these substituents [4]. Thiosemicarbazones with an extra oxygen-containing donor to make an ONS donor set have been used successfully as tridentate chelating ligands with many metal ions, including the MoO_2^{2+} core. [5]. Asymmetric molybdenum(VI) dioxo complexes of the bis(phenolate) ligands afforded high oxygen atom transfer (OAT) mechanism from dimethylsulfoxide to trimethylphosphine at 65 °C. DFT/B3LYP calculations on

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II. EXPERIMENTAL PROCEDURE

A. Materials and Physical Measurements

Microanalyses were determined on a Thermo Finnigan Flash EA 1112 Series Elemental Analyzer. UV/Visible spectra were recorded ATI-Unicam UV2 spectrophotometer. The FT-IR spectra were recorded with ATR unit by using Perkin Elmer Spectrum 400 FT Mid-IR spectrometer in the ranges of 4000–650 cm⁻¹. KBr was used for Mid-IR as the beamsplitter .The ¹H-NMR spectra were recorded on NMR spectra were obtained on a Varian INOVA 500 MHz spectrometer relative to SiMe₄ using DMSO-d₆.

B. Synthesis of the Ligand

5-chloro-4-methyl-2-hydroxybenzophenone S-methyl-4phenylthiosemicarbazone (L) was synthesized by the condensation of the 5-chloro-4-methyl-2hydroxybenzophenone and N-phenylthiosemicarbazone according to a previously published method [8], [9]. The experimental IR spectra of ligand and complex compared with the in Fig. 1.



Fig. 1. FT-IR spectra of the ligand and the dioxomolybdenum (VI) complex.

Yellow-colored solid, yield: 35%, m.p. at 171.2-172.6 °C. Anal. cal. for $C_{22}H_{20}CIN_3OS$ (409.93 g/mol), found (calc.): 65.51 (64.46) C%; 5.01 (4.92) H%; 10.22 (10.25) N%; 6.88 (7.82) S%; UV-Vis (λ_{max} (log ϵ)): 242 (4.53); 256 (4.38); 320 (3,35); 354 (4.37). ¹H-NMR: 12.90 (s, 1H, 2-OH); 8.54 (s, 1H, NH-Ph); 7.60-6.74 (12H, aromatic); 2.64 (s, 3H, 4-CH₃); 2.29 (t, 3H; S-CH₃).

C. Synthesis of the Complex

The ligand (1.0 g, 2.43 mmol) was dissolved in pyridine (2 mL). $MoO_2(acac)_2$ (0.7 g, 2.15 mmol) was added and the contents were heated at 60 °C for 5 hours. The resulting product was subjected to dry at ambient conditions. The orange precipitate was collected by filtration. Recrystallization of the product from pyridine gave the analytical-grade pure compound (Fig. 2).

Orange-colored solid, yield: 33%, m.p. at 283.8-284.1 °C. Anal. cal. for $C_{27}H_{23}CIMoN_4O_3S$ (614.95 g/mol), Found (calc.): 53.56 (52.73) C%; 3.84 (3.77) H%; 9.11 (9.11) N%; 5.12 (5.21) S%; UV-Vis (λ_{max} (log ϵ)): 222 (4.56); 258 (4.42); 314 (4.22); 344 (4.06); 420 (3.69); 588 (2.08) ¹H-NMR: 8.56 (d, 2H, C¹H, C⁵H); 7.77 (t, 1H, C³H); 7.56-6.79 (12H, aromatic); 7.35-7.36 (m, 2H, C²H, C⁴H); 2.49 (s, 3H, 4-CH₃); 1.95 (t, 3H; S-CH₃).



Fig. 2. The dioxomolybdenum (VI) complex.

III. COMPUTATIONAL DETAILS

Quantum chemical calculations were performed using the Gaussian 09W program package [10] with the Density Functional Theory applying the Becke3LYP functional and LANL2DZ basis set. The optimized geometry and

vibrational frequencies of ligand and complex were computed. Theoretical vibrational spectra of the title compounds were interpreted by means of total energy distribution (TED) with the Scale 2.0 program [11], [12]. The calculated wavenumbers in the region between 3700-3000 cm⁻¹ were scaled by 0.961 [13]. Also, probable donor-acceptor interactions of the complexes were examined with NBO analysis.

IV. RESULT AND DISCUSSION

A. NMR Spectra

The ¹H-NMR spectra of the ligand showed the expected signals arising from the protons of phenolic, aromatic ring, S-methyl, and N⁴H groups. The deprotonation of the phenolic hydroxyl and thioamide groups can be checked by the spectra. The NMR spectra of the complex clearly showed the proton signals of the coordinated second ligand (D; pyridine).

B. Structural Properties

Selected calculated bond distances, Mayer bond orders and force constants of the ligand and complex were given in Table I. After coordination, the $C=N^1$, $C=N^2$ and $C=N^4$ bond distances in the complex increase, whereas N-N bond distance in the complex decrease. The Mo=O bond lengths are 1.743 and 1.752 Å, respectively, exhibiting typical double bond character. According to the results of bond order and force constant values of Mo-N (pyridine) and Mo-N¹, these bonds show coordinative covalent bond characteristics.

Bond		Ligand			Complex	
	Distance(Å)	Bond Order	Force constant (mdyn/Å)	Distance(Å)	Bond Order	Force constant (mdyn/Å)
$C=N^1$	1.30923	1.80767455	9.4544	1.32908	1.45872357	6.7426
$C=N^2$	1.32530	1.64976265	8.7832	1.33264	1.44764168	5.3195
$C=N^4$	1.41728	0.83121717	6.0671	1.44692	0.79888874	4.5062
N-N	1.41323	0.92323489	4.5803	1.39479	0.95597784	3.6720
Mo-N(py)				2.38813	0.27452170	0.9052
Mo-O				2.00844	0.65036434	2.0866
Mo-N1				2.31241	0.29522734	1.0443
Mo-N4				2.09499	0.56775419	1.9263
Mo=O				1.74302	1.93559490	7.1619
				1.75229	1.94260986	6.8219

C. Vibrational Analysis

In the ligand's IR spectrum, the stretching vibrations of the OH, N⁴H, C=N¹ and N²=C groups were clearly observed. The v(OH) and v(N⁴H) bands disappeared in spectra of the complex due to the coordination of the deprotonated phenolate and N⁴ nitrogen. The calculated values at 941 and 915 cm⁻¹ with the TED contribution of 84% and 45%, were assigned the MoO₂ anti-symmetric and symmetric stretching wavenumbers, respectively. These modes in IR spectra were observed at 930 and 908 cm⁻¹, respectively. For the ligand, the stretching modes of C=N¹ and N²=C were calculated at 1599 and 1422 cm⁻¹ with the TED contribution of 32% and 38%, respectively. For complex, these modes were calculated at 1538 cm⁻¹ and 1452 cm⁻¹ with the TED contribution of 22% and 36%, respectively. Due to the formation of Mo-N¹ bond in complex, the C=N¹ stretching mode of complex were found to be at lower frequencies comparing with ligand. According to TED, C-S stretching modes were found at 654 cm⁻¹ for ligand and at 663 cm⁻¹ for complex. The bands were seen at 700 and 703 cm⁻¹ experimentally. (Table II) The N¹-N² stretching modes were found at 984 cm⁻¹ for ligand and at 1073 cm⁻¹ for complex. These bands were observed at 1016 and 1052 cm⁻¹ experimentally.

D. NBO Analysis

The Natural Bonding Orbital (NBO) analysis is important for the understanding of delocalization effect from the donor to the acceptor. The stabilization energy derived from the interactions between the donor and acceptor orbitals was estimated by second order perturbation interaction energy in NBO. The important interaction in the ligand having lone pair S (2) with that of anti pi bonding $C=N^2$, result the stabilization of 137.42 kcal/mol. In the complex, the stabilization energy of these interactions obtained 23.71

kcal/mol. In the complex, other important interaction is obtained lone pair N (2) (pyridine) with that lone pair Mo (1) and lone pair Mo (3), results 36.98 and 37.41 kcal/mol, respectively. The results of NBO analysis is indicate that the donor atoms transmit electron density to the Mo atom.

			Ligand	Complex		
Assignment	Experimental	Calculated	TED >(%10)	Experimental	Calculated	TED >(%10)
v(OH)	3434	3678	(100) v(O-H)			
v(NH)	3199	3369	(100) v(N-H)			
$\nu(C=N^1)$	1625	1599	(34) $v_{ring,}$ (32) $v(C-N^1)$	1600	1538	(22) δ (C-H ₃), (22) ν (C-N ¹), (21) ν _{ring}
v(C=N ²)	1543	1422	(38) v(C-N ²), (23)NH rock , (14) v _{ring}	1546	1452	(36) v(C-N ²), (14) δ(C-H ₃), (13) v(C=N)
δ(COH) ν (CO)	1251/1229	1139	(28) δ (COH),(25) v_{ring} (18) δ_{ring} ,(12) v (C-O)			
v(C-S)	700	654	(69) v(C-S)	703	663	(68) v(C-S)
v (N-N)	1016	984	$(53)v(N-N),(14) v_{ring}$	1052	1073	(37) v(N-N), (13) v_{ring}
v(MoO ₂)asym				930	941	(84) v(Mo=O)
$\nu(MoO_2)$ sym				908	915	(45) ν(Mo=O), (28) γ(CH) _{ring}

V. CONCLUSION

New dioxomolybdenum(VI) complex with 5-chloro-4methyl-2-hydroxybenzophenone S-methyl-4-phenyl thiosemicarbazone have been characterized by analytical method and spectroscopic data and molecular structure analyses of pyridine coordinated complex. The ligand coordinated to the metal centers in the similar approach of ONN donor. Due to the neglect of vibrational anharmonicity and hydrogen bonding effect, the deviation of between calculated wavenumbers and experimental wavenumbers were higher in the region 4000-3000 cm⁻¹ than 3000-400 cm⁻¹ ¹. The deviations in the corresponding regions were found to be below 100 cm⁻¹. Experimental and calculated wavenumbers were found to be in a good agreement. Finally, some chemical properties, like structural parameters and frequency vibrations, obtained from calculations and experimental data were in accordance with each other.

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REFERENCES

- M. D. Shoeili, M. Boghaei, M. Amini, M. Bagherzadeh, and B. Notash, "New molybdenum(VI) complex with ONS-donor thiosemicarbazone ligand: Preparation, structural characterization, and catalytic applications in olefin epoxidation," *Inorg. Chem. Commun.*, vol. 27, pp. 26-30, 2013.
- [2] J. Pisk, B. Prugovečki, D. Matković Čalogović, R. Poli, D. Agustin, and V. Vrdoljak, "Charged dioxomolybdenum(VI) complexes with pyridoxal thiosemicarbazone ligands as molybdenum(V) precursors in oxygen atom transfer process and epoxidation (pre)catalysts," *Polyhedron*, vol. 33, pp. 441-449, 2012.
- [3] H. G. Zhang, "Preparation, characterization, and crystal structures of dioxomolybdenum(VI) complexes with tridentate Schiff base ligands," *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, vol. 43, pp. 933-936, 2013.

- [4] D. Eierhoff, W. C. Tung, A. Hammerschmidt, and B. Krebs, "Molybdenum complexes with O, N, S donor ligands as models for active sites in oxotransferases and hydroxylases," *Inorganica Chimica Acta*, vol. 362, pp. 915-928, 2009.
- [5] J. R. Dilworth and R. Hueting, "Metal complexes of thiosemicarbazones for imaging and therapy," *Inorg. Chim. Acta*, vol. 389, pp. 3-15, 2012.
- [6] M. R. Pedrosa, J. Escribano, R. Aguado, V. Diez, R. Sanz, and F. J. Arnaiz, "Dinuclear oxomolybdenum(VI) acetylacetonates: Crystal and molecular structure of $Mo_2O_5(acac)_2L_2$ (L = D₂O, DMF)," *Polyhedron*, vol. 26, pp. 3695-3702, 2007.
- [7] R. Mayilmurugan, B. N. Harum, M. Volpe, A. F. Sax, M. Palaniandavar, and N. C. Mösch-Zanetti, "Mechanistic insight into the reactivity of oxotransferases by novel asymmetric dioxomolybdenum(VI) model complexes," *Chem. Eur. J.*, vol. 17, pp. 704-713, 2011.
- [8] B. İ. Ceylan, Y. D. Kurt, and B. Ülküseven, "Synthesis and characterization of dioxomolybdenum(VI) chelates with dibasic form of 5-bromo-2-hydroxybenzophenone-S-methyl/ethyl/4-phenylthiosemicarbazones," *Rev. Inorg. Chem.*, vol. 29, no. 1, pp. 50-67, 2009.
- [9] B. İ. Ceylan, Y. D. Kurt, and B. Ülküseven, "Synthesis and characterization of new dioxomolybdenum(VI) complexes derived from benzophenone-thiosemicarbazone (H₂L). Crystal structure of [MoO₂L(PrOH)]," J. Coord. Chem., vol. 62, no. 5, pp. 757-766, 2009.
- [10] G. Scalmani et al., Gaussian 09, Revision A.02, Gaussian Inc., Wallingford CT, 2009.
- [11] G. Pongor, Department of Theoretical Chemistry, Scale 2, Edvös Lorand University, Budapest, 1978.
- [12] G. Pongor, G. Fogarasi, I. Magdo, J. E. Boggs, G. Keresztury, and I. S. Ignatyev, "Theoretical prediction of vibrational spectra, a priori scaled quantum mechanical (SQM) force field and vibrational spectra of pyrimidine," *Spectrochim. Acta*, vol. 48 A, pp. 111-119, 1992.
- [13] NIST. (May 2015). Precomputed vibrational scaling factors. [Online]. Available: http://cccbdb.nist.gov/vibscalejust.asp.



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