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단신

세자리 O,N,S-주개 Schiff 염기와 4,4'-Bipyridyl 리간드의 Dioxomolybdenum(VI) 착물의 합성과 특성

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Synthesis and Characterization of Dioxomolybdenum(VI) Complexes with Tridentate O,N,S-Donor Schiff Bases and 4,4'-Bipyridyl Ligand

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Molybdenum chemistry has received the intense attention because of its relevance to the active sites of molybdoenzymes. The presence of the *cis*-dioxomolybdenum (VI) cation, $[MoO_2]^{2+}$, in the oxidized forms of certain molybdoenzymes has stimulated both the search for new structures in which this moiety is coordinated to ligands containing nitrogen, oxygen and/or sulfur donors and also the study of their chemical, spectroscopic, electrochemical and structural properties.[1-5]

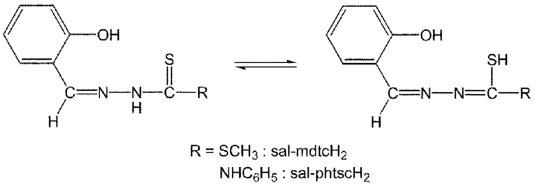
Tridentate ONS-chelating ligands derived from thiosemicarbazide or dithiocarbazate of salicylaldehyde have been widely used in much of this work.[6-9] The tautomerism (*Scheme* 1) of these ligands as well as the well known tendency of sulfur donors to act as bridging ligands allows various structural possibilities for the corresponding metal complexes.

As part of our studies on the coordination chemistry of d-block metal complexes with Schiff base ligands, we have earlier described the synthesis and spectroscopic and electrochemical properties for the molybdenum(VI) complexes, such as $[MoO_2L(MeOH)]$ [L=salicylaldehyde S-methyldithiocarbazate (sal-mdtc^{2-}) or salicylaldehyde N-phenylthio semicarbazate (sal-phtsc^{2-})] and $[Mo_2O_4L_2]$ (L=salicylaldehyde 2-amino-4-*t*-butyl phenol) in previous paper.[10,11] However, the mononuclear dioxomolybdenum(VI) complexes containing the tridentate Schiff base and 4,4'-bipyridyne (4,4'-bpy) or 4,4'-dipyridyl dioxide (4,4'-dpdo) are not very familiar and not adequately explored. Recently, dioxomolybdenum(VI) complex, $[MoO_2(\text{sal-mdtc})(CH_3OH)]$(4,4'-bpy) has been prepared by *Vrdoljak et al.* in 2005.[12] In this paper, we report the synthesis and crystal structure on new dioxomolybdenum(VI) complexes **1-3**.

EXPERIMENTAL SECTION

All the reagents and solvents employed were commercial and used without further purification. The Schiff bases, sal-mdtcH$_2$ and sal-phtscH$_2$, were prepared by the literature methods.[13]

C. H. N. for the complexes were analyzed by using a Carlo-Erba EA-1106R. The IR spectra of



Scheme 1. The tautomerism of Schiff base ligands.

solid samples in ATR method were recorded on a JASCO FT-IR 4100 type A. The ^{1}H-NMR spectra in DMSO-d_6 were recorded on a Varian AS 400 MHz spectrometer and referenced to TMS (internal). Electronic spectra were obtained on a Milton Roy Genesys 2 UV/Vis. spectrophotometer. TG analysis was performed on a Shimadzu DTG-60 instrument with a heating rate of 10 °C min^{-1}.

[MoO$_2$(sal-mdtc)(CH$_3$OH)](4,4'-bpy) (1). The reaction mixture of MoO$_2$(acac)$_2$ (0.68 mmol, 0.223 g) and sal-mdtcH$_2$ (0.68 mmol, 0.153 g) in methanol solution (15 mL) was refluxed for 2 h. and to the solution was added 4,4'-bpy (0.68 mmol, 0.106 g) with stirring. The mixture was further refluxed for another 1 h. and filtered. The filtrate was left in ambient temperature for several days. The reddish crystals suitable for X-ray diffraction were isolated in 4.6% (0.017 g) yield. Anal. Calcd. for $C_{20}H_{20}N_4O_4S_2Mo$: C, 44.44; H, 3.73; N, 10.37; S, 11.87. Found: C, 44.32; H, 3.65; N, 10.32; S, 11.93. UV-Vis (DMF) [λ_{max} nm(log ε)]: 400 (4.03), 364 (4.15), 316 (4.35), 268 (4.34), 250 (4.24), 226 (4.20). Significant IR bands (cm^{-1}): 3680(w), 2973(s), 2866(m), 1597(s), 1588(s), 1548(m), 1488(m), 1277s) 1055(s), 1032(vs), 1016(s), 971(w), 916(s), 893(vs), 835(m), 803(m), 761(m), ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.60 (s, S-$\underline{CH}_3$, 3H), 3.17 (d, $\underline{CH}_3$OH, 3H, *J*=5.2 Hz), 4.11 (q, CH$_3\underline{OH}$, 1H, *J*=5.2 Hz), 6.96 (d, 1H, *J*=8.4 Hz), 7.08 (t, 1H, *J*=7.2 Hz), 7.57 (t, 1H, *J*=7.6 Hz), 7.78 (d, 1H, *J*=7.6 Hz), 7.83 (d, -NCH$\underline{CH}$-, 4H, *J*=5.6 Hz), 8.73 (d, -N$\underline{CH}$CH-, 4H, *J*=5.2 Hz), 8.95 (s, N=$\underline{CH}$, 1H).

The compounds **2** and **3** were prepared similarly, by the method for the preparation of **1**, with use of an appropriate tridentate Schiff base and 4,4'-dpdo, respectively.

Analytical data for the complexes are as follow;

[MoO$_2$(sal-mdtc)(H$_2$O)](4,4'-dpdo) (2). Yield (crude): 35% (0.132 g). Anal. Calcd. for $C_{19}H_{18}N_4O_6S_2Mo$: C, 40.86; H, 3.25; N, 10.03; S, 11.48. Found: C, 40.53; H, 3.42; N, 10.04; S, 11.88. UV-Vis (DMF) [λ_{max} nm(log ε)]: 402 (3.82), 348 (4.67), 264 (4.19), 246 (4.18), 234 (4.15), 222 (4.14), 213 (4.14). Significant IR bands (cm^{-1}): 3376(w), 3104(w), 1601(m), 1587(m), 1550(m), 1470(m), 1217(vs), 1175(s), 1028(m), 973(m), 924(vs), 885(vs), 860(vs), 752(vs). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.67(s, S-$\underline{CH}_3$, 3H), 3.34(s, H$_2$O, 2H), 6.95 (d, 1H, *J*=8.4 Hz), 7.08 (t, 1H, *J*=7.4 Hz), 7.57 (t, 1H, *J*=7.8 Hz), 7.78 (d, 1H, *J*=8.0 Hz), 7.89 (d, -NCH$\underline{CH}$-, 4H, *J*=6.8 Hz), 8.30 (d, -N$\underline{CH}$CH-, 4H, *J*=6.8 Hz), 8.95 (s, N=$\underline{CH}$, 1H).

[MoO$_2$(sal-phtsc)(H$_2$O)](4,4'-dpdo) (3). Yield (crude): 80% (0.334 g). Anal. Calcd. for $C_{24}H_{21}N_5O_6SMo$: C, 47.77; H, 3.51; N, 11.61; S, 5.31. Found: C, 48.01; H, 3.75; N, 11.92; S, 5.67. UV-Vis (DMF) [λ_{max} nm(log ε)]: 430 (3.39), 346 (4.72), 268 (4.25), 232 (4.13), 220 (4.23), 208 (4.12). Significant IR bands (cm^{-1}): 3252(w), 3122(w), 3095(w), 3060(w), 3026(w), 1595(m), 1552(m), 1496(s), 1471(s), 1436(s), 1253(s), 1209(s), 1174(s), 1027(m), 922(s), 889(vs), 825(vs), 758(s), 697(s). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.34 (s, H$_2$O, 2H), 6.90 (d, 1H, *J*=8.4 Hz), 7.01 (q, 2H, *J*=7.7 Hz), 7.30 (t, 2H, *J*=7.5 Hz), 7.47 (t, 1H, *J*=7.7 Hz), 7.69 (d, 1H, *J*=7.8 Hz), 7.74 (d, 2H, *J*=7.8 Hz), 7.89 (d, -NCH$\underline{CH}$-, 4H, *J*=7.2 Hz), 8.30 (d, -N$\underline{CH}$CH-, 4H, *J*=7.2 Hz), 8.81 (s, N=$\underline{CH}$, 1H), 9.68 (s, -$\underline{NH}$-Ph, 1H).

Unfortunately, it was failed to grow diffraction quality crystals for complexes **2** and **3**.

Crystal structure determination of 1. Single crystals of **1** were obtained by the method described in the above. Structural measurement was performed on an ADSC Quantum 210 detector at Beamline 4A MXW of Pohang Light Source using λ=0.76999 Å radiation with a detector-to-crystal distance of 6.0 cm. The unit cell parameters were calculated by least-squares fit of 7423 reflections in the range of $1.83 < \theta < 27.77°$. The structure was solved by direct method[14] and refined on F^2 by full-matrix least-squares procedures.[15] All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor cal-

Table 1. Crystal data and structure refinement for **1**

Compound	1
Empirical formula	$C_{20}H_{20}N_4O_4S_2Mo$
Fw	540.48
Temp. (K)	293(2)
λ(Å)	0.76999
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	6.989(1)
b(Å)	17.473(4)
c(Å)	14.622(3)
β(°)	100.28(3)
V(Å^3)	1757.0(6)
Z	4
$D_{calc.}$(Mg/m^3)	1.748
μ (mm^{-1})	1.010
F(000)	932
Theta range for data collection	1.83 to 27.77°
Index ranges	0<=h<=8, -22<=k<=22, -19<=l<=18
Reflections collected	7423
Independent reflections	3828 [R(int) = 0.0458]
Completeness to theta=26.99°	92.4%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3828/0/229
Goodness-of-fit on F2	1.064
Final R indices [I>2sigma(I)]	R_1=0.0324, wR_2=0.0829
R indices (all data)	R_1=0.0344, wR_2=0.0841
Largest diff. peak and hole (eÅ^{-3})	0.824 and -1.319

culation at idealized positions by using a riding model, but not refined. A summary of crystal data and structure refinement for the compound **1** is listed in *Table* 1.

RESULTS AND DISCUSSION

The reaction of $MoO_2(acac)_2$ with the Schiff base ligands, which are derived from salicylaldehyde and S-methyldithiocarbazate,[16] or 4-phenylthiosemicarbazide and 4,4'-bpy or 4,4'-dpdo in methanol solution give a monomeric dioxomolybdenum(VI) complexes **1-3**, respectively. It is likely that the coordinated water molecule in the complexes **2** and **3** stems from the trace of reactants. All complexes are air stable in the solid state and have poor solubilities in the common organic solvents, but they are highly soluble in DMF and DMSO. The formulations are in accordance with the data of elemental analysis and physicochemical measurements. The oxidation state of Mo as expected from overall charge considerations for the complexes is +6.

Spectral properties. The electronic spectra for all complexes exhibit the bands at *ca.* 410 nm (log ε=*ca.* 3.75) assigned as charge transfer transition from oxygen orbital to a metal *d*-orbital.[10,11] Since molybdenum(VI) ion has no d electron, absorption bands of pure d-d origins are not expected to appear. The bands observed below 364 nm (log ε= 4.12~4.72) are due to intraligand transitions compared to the spectra of free ligands. Infrared spectra for the complexes **1-3** show two intense absorption peaks at ~889 and ~921 cm^{-1}. These bands are assigned to the asymmetric and the symmetric stretching vibration of *cis*-MoO_2 group, respectively, by comparison with the spectra reported previously.[17] For all complexes an intense vibration associated with the C=N stretching frequency is observed at ~1598 cm^{-1},[17a,18] which is shifted to low frequency compared to ~1620 cm^{-1} of the free ligands, indicating that the azomethine nitrogen atom is coordinated to the molybdenum center. The complexes exhibit weak bands at ca. 3436 and 3122 cm^{-1} due to the presence of coordinated methanol or water molecules and phenyl imine, respectively.[17] The existence of methanol or water molecule binding to MoO_2 group is also supported from the results of ^{1}H-NMR measurement. The ^{1}H-NMR spectra show the proton resonances at 3.17 and 4.11 ppm for methyl and OH group of methanol for **1**.[6] For complexes **2** and **3**, the proton resonances for water molecule are observed at 3.34 ppm, respectively. In addition, the complex **1** exhibits N=CH proton resonance at 8.95 ppm, two different 4,4'-bpy proton signals at two different positions (8.73 ppm for $N\underline{CH}CH$ and 7.83 ppm for $NCH\underline{CH}$), aromatic proton bands at 6.96~7.78 ppm, and S-CH_3 proton resonance at 2.60 ppm, respectively.[6,11,13a] In all complexes, the ratio of integrated intensities for the proton signals of Schiff base and 4,4'-bpy or 4,4'-dpdo consistent with the stoichiometric ratio 1 : 1. ^{1}H-NMR data of other complexes are given in the experimental section. The complexes of **2** and **3** show similar ^{1}H-NMR spectra to the complex of **1**, except appearing the proton resonances for the phenyl amine of sal-phtsc ligand (for **3**) instead of disappearing the proton resonances for the methyl group of sal-mdtc ligand. The azomethine proton resonances (8.95 ppm for **1** and **2**, and ppm 8.81 for **3**) in all complexes are shifted to down field compared to the resonances (8.53 ppm for sal-mdtcH$_2$ and 8.49 ppm for sal-phtscH$_2$) of the free ligands. Also, the signals for one OH proton (13.34 ppm for sal-mdtcH$_2$ and 11.78 ppm for sal-phtscH$_2$) and the NH proton (10.24 ppm for sal-mdtcH$_2$ and 10.05 and 9.98 ppm for sal-phtscH$_2$) of free Schiff base ligand are found to disappear in the spectra of the complexes. These NMR data imply that the Schiff base ligand coordinates to the MoO$_2$ group in the thiolate form.

Thermal properties. The thermogravimetric analyses (TGA) of complexes **1-3** are conducted in the temperature range of 30-700 °C with a 10 °C/min temperature interval. The TG curves exhibit four steps of weight losses, which are the release of the solvent molecule, two-step decompositions of organic ligands, and the formation of the molybdenum trioxide. TG curve for a representative complex **1** is shown in *Fig.* 1. Complex **1** undergoes a rapid weight loss of 5.32% from 80 to 102 °C, due to the release of CH$_3$OH molecule (calculated: 5.93%). The total weight loss of 69.14% by two step decompositions, which are a significant weight loss of 29.78% from 184 to 257 °C and a gradual weight loss of 39.36% between 257 and 593 °C is attributable to the concomitant release of the 4,4'-bpy and sal-mdtc organic ligands, with a calculated value of 70.40%. For the complexes **2** and **3**, the release of coordinated water molecule occurs in the temperature range of 30~128 °C with the weight loss of 2.86% (calculated 3.22%) and of 220~232 °C with the weight loss of 2.99% (calculated 2.99%), respectively. The organic ligands decompose in the range of 189~639 °C with weight loss of 72.45% (calculated 73.87%) for **2** and of 232~619 °C with the weight loss of 74.25% (calculated 75.78%) for **3**, respectively. For each complexes, the wt% value of the final residues are accordance with that of molybdenum trioxide.

Structural description of 1. The molecular structure of complex **1** is shown in *Fig.* 2. Selected bond lengths and angles are listed in *Table* 2. The compound consist of two independent moieties: [[MoO$_2$(sal-mdtc)(CH$_3$OH)] and uncoordinated 4,4'-bpy molecule. In the complex, the tridentate Schiff base ligand, sal-mdtc^{2-} is bonded to the *cis*-$[\mathrm{Mo(VI)O_2}]^{2+}$ core on a meridional plane through the phenolate-O, the imine -N, and the deprotonated thiolate-S atoms forming one five- and one six-membered chelate ring. The sixth coordination site around Mo is occupied by a solvent methanol molecule, thereby providing a distorted octahedral coordination environment around Mo. In general the structure resemble those of the *cis*-dioxomolybdenum (VI) complexes with tridentate Schiff base ligand have been prepared previously in our laboratory.[10] However, it is distinguished from the previous complexes that one uncoordinated 4,4-bpy

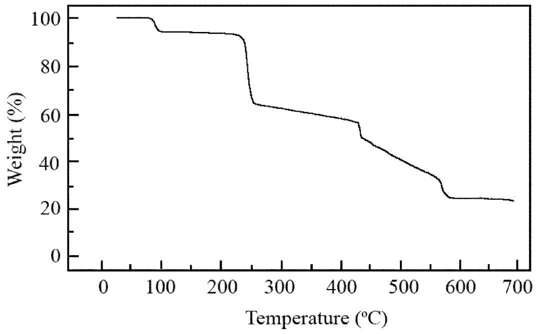


Fig. 1. TG curve of complex 1.

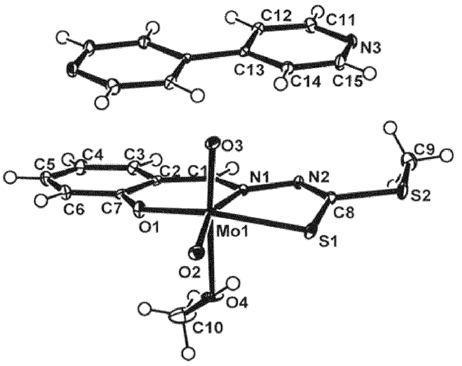


Fig. 2. ORTEP III[22] drawing of complex 1.

Table 2. Selected bond lengths (Å) and angles (°) for complex 1

Complex **1**			
Mo(1)-O(1)	1.938(2)	Mo(1)-O(2)	1.716(2)
Mo(1)-O(3)	1.709(2)	Mo(1)-O(4)	2.275(2)
Mo(1)-N(1)	2.269(2)	Mo(1)-S(1)	2.433(1)
S(1)-C(8)	1.751(2)	O(1)-C(7)	1.336(2)
C(7)-C(2)	1.410(3)	C(2)-C(1)	1.444(3)
N(1)-C(1)	1.303(3)	N(1)-N(2)	1.409(2)
N(2)-C(8)	1.290(3)	O(4)-C(10)	1.407(3)
N(3)-C(11)	1.341(3)	N(3)-C(15)	1.337(3)
O(2)-Mo(1)-O(3)	105.13(8)	O(2)-Mo(1)-O(1)	105.15(7)
O(3)-Mo(1)-O(1)	98.45(7)	O(2)-Mo(1)-N(1)	159.39(7)
O(3)-Mo(1)-N(1)	92.34(7)	O(1)-Mo(1)-N(1)	82.50(6)
O(2)-Mo(1)-O(4)	84.76(7)	O(3)-Mo(1)-O(4)	169.83(7)
O(1)-Mo(1)-O(4)	80.84(7)	N(1)-Mo(1)-O(4)	77.51(6)
O(2)-Mo(1)-S(1)	90.71(6)	O(3)-Mo(1)-S(1)	95.87(5)
O(1)-Mo(1)-S(1)	154.94(5)	N(1)-Mo(1)-S(1)	76.45(5)
O(4)-Mo(1)-S(1)	81.45(5)		

molecule is present per asymmetric structural unit.

In the complex **1**, the average Mo=O bond length (1.713(2)Å) and the O=Mo=O bond angle (105.13(8)°) are typical for *cis*-MoO_2 group.[10b,19] The bond lengths for Mo-S (2.433(1)Å) and Mo-N1 (2.269(2)Å) are also similar to those reported for other complexes.[10b,19] The *cis*- and *trans*- L-Mo-L angles are in the range of 76.45(5)-105.15(7)° and 154.94(5)-169.83(7)°, respectively. To a large extent these distortions stem from the incorporation of Mo into a five-membered ring. The bond lengths, N1-C1 (1.303(3)Å) and N2-C8 (1.290(3)Å) indicate that these are double bonds, respectively (normal single bond is 1.364Å).[10b] The Mo-O4 bond length (2.275(2)Å) is relatively long due to the *trans* effect[20] of the terminal oxide ligands and the coordinated solvent molecule (CH_3OH) is labile. The metric parameters for the five- and six-membered ring are unexceptional and compare closely to those in related molecules.[10b] Also, the metric parameters for 4,4'-bpy are similar to those in related molecules.[21]

CONCLUSIONS

The initial goal of this work was to synthesis the di- or tetra-nuclear oxomolybdenum complexes, $[Mo_2O_4(\text{Schiff base})(L)]$ or $[Mo_4O_4(\text{Schiff base})_4(L)_2]$ (Schiff base = sal-mdtc^{2-} or sal-phtsc^{2-} and L = 4,4'-bpy or 4,4'-dpdo), by the reaction of $MoO_2(acac)_2$ with tridentate Schiff base and neutral bidentate which it is possible to act as bridging ligand under an appropriate reaction condition. Unfortunately, the treatment of $MoO_2(acac)_2$ with equimolar of Schiff base and bidentate ligand in methanol led to the mononuclear dioxomolybdenum(VI) complexes of the type of $[MoO_2(\text{Schiff base})(S)](L)$ (S=CH_3OH or H_2O). However, these three dioxomolybdenum(VI) complexes synthesized in this work contain one uncoordinated 4,4'-bpy or 4,4'-dpdo molecule per asymmetric structural unit. This structure is not common and it is noteworthy.

Supporting information available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-685825 (**1**)). The data can be obtained free of charge via www.ccdc.cam. ac.uk/conts/ retrieving. html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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