

Synthesis and Characterizations of Dinuclear Dioxomolybdenum(VI) Complexes with Thiocarbohydrazides of Salicylaldehyde, Bridged by 4,4'-Dipyridyl or Its Derivatives

Bon Kweon Koo,^{*} Haesung Kang, and Woo Taik Lim[†]

Department of Chemistry, Catholic University of Daegu, Gyeongsan, Gyeongbuk 712-702, Korea. *E-mail: bkkoo@cu.ac.kr

[†]Department of Applied Chemistry, Andong National University, Andong, Gyeongbuk 760-749, Korea

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Molybdenum chemistry has received intense attention because of its biochemical role in metalloenzymes and its rich chemistry. It is well-known that molybdenum as a constituent of enzymes participates in redox reactions, e.g. oxidation of sulfide, aldehydes, xanthine and other purines,¹ and reduction of nitrate to molecular nitrogen.² In the oxidized forms of certain molybdoenzymes, the presence of the *cis*-dioxomolybdenum(VI) cation, [MoO₂]²⁺ 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.³⁻⁷

Tridentate ONS-chelating schiff base ligands derived from thiosemicarbazide or dithiocarbamate of salicylaldehyde have been widely used in much of this work.⁸⁻¹¹ 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 reported the synthesis and spectroscopic and electrochemical properties for the dioxomolybdenum(VI) complexes, such as [MoO₂L(MeOH)] [L = salicylaldehyde N-phenylthiosemicarbazate (sal-phtsc²⁻) or salicylaldehyde S-methyldithiocarbamate (sal-mdtc²⁻)] and [Mo₂O₄L₂] (L = salicylaldehyde 2-amino-4-*t*-butylphenol).^{12,13} The oxomolybdenum complexes with dibasic tridentate schiff bases are of the type: monomeric-[MoO₂(L)(S)] (L = schiff base, S = monodentate neutral ligand), which is dominant, or dimeric-[MoO(μ-O)(L)]₂ with asymmetric double oxygen bridge, or polymeric with single oxygen bridge.¹⁴ However, the linear diamine/diimine-bridged dinuclear oxomolybdenum(VI) complexes are not very familiar and not adequately explor-

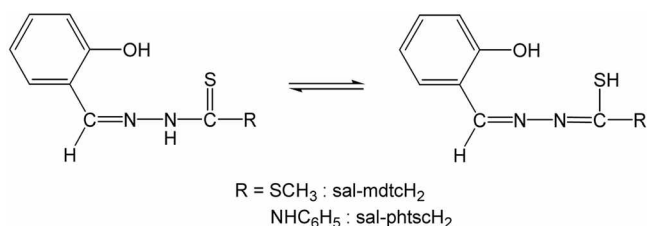
ed.¹⁵ In this paper, we report the synthesis and crystal structure on some new dimeric dioxomolybdenum(VI) complexes containing schiff base and 4,4'-bipyridyne (4,4'-bpy), *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe), or 4,4'-dipyridyl-dioxide (4,4'-dpdo) ligands which is directional and can be established multinuclear compound.

Experimental Section

All the reagents and solvents employed were commercial and used without further purification. The schiff bases, sal-mdtcH₂ and sal-phtscH₂, were prepared by the literature methods.¹⁶

C. H. N. for the complexes were analyzed by using a Carlo-Erba EA-1106R. The IR spectra of solid samples in ATR method were recorded on a JASCO FT-IR 4100 type A. The ¹H-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. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu DTG-60 instrument with a heating rate of 10 °C min⁻¹.

[Mo₂O₄(sal-mdtc)₂(4,4'-bpe)] (1). The reaction mixture of MoO₂(acac)₂ (0.68 mmol, 0.223 g) and sal-mdtcH₂ (0.68 mmol, 0.153 g) in dichloromethane (15 mL) solution was refluxed for 2 h and to the solution was added 4,4'-bpe (0.34 mmol, 0.062 g). The mixture was further refluxed for another 1 h. The precipitate was filtered and the filtrate was left in room temperature for several days. The reddish crystalline was collected by suction filtration, washed with diethyl ether, and dried in vacuum oven. Yield: 57% (0.172 g) based on Mo. Anal. Calcd. for C₃₀H₂₆N₆O₆S₄Mo₂: C, 40.64; H, 2.96; N, 9.48; S, 14.47. Found: C, 40.75; H, 3.03; N, 9.43; S, 14.67. UV-Vis (DMF) [λ_{max} nm (log ε)]: 400 (3.98), 367 (4.23), 352 (4.26), 313 (4.54), 301 (4.63), 265 (4.62), 259 (4.34), 253 (4.30), 229 (4.13), 220 (4.22), 208 (4.17). Significant IR bands (cm⁻¹): 3062 (w), 1609 (m), 1600 (s), 1551 (s), 1492 (m), 1424 (w), 1273 (m), 1013 (w), 980 (m), 926 (s), 890 (vs), 885 (s), 830 (m), 751 (m). ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.56 (s, S-CH₃, 6H), 6.92 (d, ArH, 2H, *J* = 8.4 Hz), 7.04 (t, ArH, 2H, *J* = 7.4 Hz), 7.51 (s, -NCH=CH-, 2H), 7.55 (t, ArH, 2H), 7.57 (d, -NCHCH-



Scheme 1. The tautomerism of schiff base ligands.

4H), 7.74 (d, 2H, $J = 7.7$ Hz), 8.57 (d, -NCHCH-, 4H, $J = 4.8$ Hz), 8.92 (s, N=CH, 2H). The reddish crystals, $[\text{Mo}_2\text{O}_4(\text{sal-mdtc})_2(4,4'\text{-bpe})](\text{CH}_3\text{OH})$ (**2**), suitable for X-ray diffraction were obtained by slow diffusion of methyl alcohol into a dichloromethane solution. Yield: 15% (0.046 g). Anal. Calcd. for $\text{C}_{31}\text{H}_{30}\text{N}_6\text{O}_7\text{S}_4\text{Mo}_2$: C, 40.53; H, 3.29; N, 9.15; S, 13.96. Found: C, 39.96; H, 3.21; N, 9.18; S, 13.85.

$[\text{Mo}_2\text{O}_4(\text{sal-mdtc})_2(4,4'\text{-bpy})]$ (**3**). The compound was prepared similarly by the method described above for the preparation of **1**, with use of 4,4'-bpy instead of 4,4'-bpe. Yield: 65% (0.190 g). Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_6\text{O}_6\text{S}_4\text{Mo}_2$: C, 39.07; H, 2.81; N, 9.76; S, 14.90. Found: C, 38.93; H, 2.87; N, 9.80; S, 15.34. UV-Vis (DMF) [λ_{max} nm (log ϵ): 406 (3.90), 349 (4.32), 319 (4.35), 265 (4.56), 256 (4.21), 250 (4.16), 244 (4.11), 235 (4.16), 226 (4.05), 214 (4.13). Significant IR bands (cm^{-1}): 3071 (w), 1597 (m), 1587 (s), 1549 (s), 1485 (m), 1435 (w), 1275 (m), 1223 (w), 1028 (w), 981 (m), 923 (s), 894 (vs), 809 (m), 750 (m). ^1H NMR (400 MHz, DMSO- d_6): δ 2.60 (s, S-CH₃, 6H), 6.95 (d, ArH, 2H, $J = 8.4$ Hz), 7.06-7.10 (m, ArH, 2H), 7.54-7.59 (m, ArH, 2H), 7.78 (dd, ArH, 2H, $J = 7.8$ Hz, 1.4 Hz), 7.83 (dd, -NCHCH-, 4H, $J = 4.4$ Hz, 1.6 Hz), 8.73 (dd, -NCHCH-, 4H, $J = 4.4$ Hz, 1.6 Hz), 8.95 (s, N=CH, 2H).

$[\text{Mo}_2\text{O}_4(\text{sal-phtsc})_2(4,4'\text{-dpdo})]$ (**4**). The compound was prepared similarly by the method described above for the preparation of **1**, with use of 4,4'-dpdo and sal-phTscH₂ instead of 4,4'-bpe and sal-mdtcH₂, respectively. Yield: 60% (0.200 g). Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{N}_8\text{O}_8\text{S}_2\text{Mo}_2$: C, 46.44; H, 3.08; N, 11.40; S, 6.53. Found: C, 46.10; H, 3.08; N, 10.59; S, 6.33. UV-Vis (DMF) [λ_{max} nm (log ϵ): 436 (3.71), 346 (4.78), 268 (4.54), 244 (4.35), 214 (4.22). Significant IR bands (cm^{-1}): 3260 (w), 3117 (w), 1597 (s), 1559 (m), 1513 (vs), 1474 (m), 1438 (vs), 1318 (m), 1272 (m), 1212 (vs), 1174 (m), 924 (s), 893 (vs), 860 (m), 830 (vs), 747 (vs), 686 (m). ^1H NMR (400 MHz, DMSO- d_6): δ 6.90 (d, ArH, 2H, $J = 8.4$ Hz), 6.98-7.05 (m, ArH, 4H), 7.28-7.33 (m, ArH, 4H), 7.47 (ddd, ArH, 2H, $J = 9.0$ Hz, 6.8 Hz, 1.6 Hz), 7.69 (dd, ArH, 2H, $J = 7.8$ Hz, 1.8 Hz), 7.73-7.76 (m, ArH, 4H), 7.87-7.90 (m, -NCHCH-, 4H), 8.28-8.32 (m, -NCHCH-, 4H), 8.81 (s, N=CH, 2H), 9.68 (s, Ph-NH, 2H).

Crystal structure determination of 2. X-ray diffraction data of the single-crystal was collected at 293(2) K on an ADSC Quantum 210 detector at Beamline 4A MXW of Pohang Light Source. The crystal evaluation and data collection were done using 0.76999 Å-wavelength radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 second per frame. We got basic scale file from program HKL2000 (Otwinowski & Minor, 1997). The reflections were successfully indexed by the automated indexing routine of the DENZO program. A total of 3,695 reflections were harvested by collecting 72 sets of frames with 5° scans with an exposure time of 1 second per frame. This highly redundant data set was corrected for Lorentz and polarization effects, and a negligible correction for crystal decay was also applied. The space group R-3 was determined

Table 1. Crystal data and structure refinement for **2**

Empirical formula	C ₃₁ H ₃₀ Mo ₂ N ₆ O ₇ S ₄
Fw	918.76
Temp. (K)	293(2)
λ (Å)	0.76999
Crystal system	Rhombohedral
Space group	R-3
a (Å)	14.5143(17)
a (°)	102.790(17)
V (Å ³)	2787.8(6)
Z	3
D _{calc} (Mg/m ³)	1.699
μ (mm ⁻¹)	0.957
F(000)	1440
Theta range for data collection	1.63 to 30.40°
Index ranges	$-1 \leq h \leq 19$, $-14 \leq k \leq 11$, $-14 \leq l \leq 11$
Reflections collected/unique	3695 / 3695 [R(int) = 0.0000]
Completeness to theta = 30.40°	83.3%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3695 / 0 / 238
Goodness-of-fit on F ₂	1.116
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1006$, $wR_2 = 0.2543$
R indices (all data)	$R_1 = 0.1006$, $wR_2 = 0.2543$
Largest diff. peak and hole	3.089 and -1.809 e.Å ⁻³

ed by the program XPREP (ver. 6.12, Bruker-AXS). The structure was solved by direct method¹⁷ and refined on F^2 by full-matrix least-squares procedures.¹⁸ All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using riding model, but not refined. A summary of the experimental and crystallographic data for compound **2** is presented in Table 1.

Results and Discussion

The reaction of $\text{MoO}_2(\text{acac})_2$ with the schiff base ligands which are derived from salicylaldehyde and S-methyldithiocarbamate¹⁹ or 4-phenylthiosemicarbazide with respective 4,4'-bpy, 4,4'-bpe, and 4,4'-dpdo in dichloromethane solution gave a dimeric dioxomolybdenum(VI) complexes **1-4**, respectively. All complexes are air stable in the solid state and have poor solubilities in 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 complexes show similar electronic spectra, suggesting that they have essentially similar structure. Since molybdenum(VI) ion has no d electron, absorption bands of pure d-d origins are not expected to appear. The bands at ca. 414 nm (log $\epsilon =$ ca. 3.86) for all complexes may possibly be assigned as charge transfer transition from oxygen orbital to a metal d -orbital.^{12,13} On the other hand, the bands observed below 367 nm are due to intraligand transitions of sal-mdtc or sal-phtsc ligands.

Infrared spectra for the complexes **1-4** show two intense absorption peaks at *ca.* 892 and *ca.* 924 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.²⁰ For all complexes an intense vibration associated with the C=N stretching frequency is observed at *ca.* 1601 cm^{-1} ,^{20a,21} which is shifted to low frequency compared to *ca.* 1620 cm^{-1} of the free ligands, indicating that the azomethine nitrogen atom is coordinated to the molybdenum center. The complex **4** exhibits weak band at 3260 cm^{-1} due to the NH stretching vibration of salphtsc ligand.²⁰ The ligands binding to MoO_2 group are also supported from the results of $^1\text{H-NMR}$ measurements. The $^1\text{H-NMR}$ spectra for the complex **1** exhibits N=CH proton resonance at 8.92 ppm, three different 4,4'-bpe proton resonances at three different positions (8.57 ppm for NCHCH, 7.57 ppm for NCH $\bar{\text{C}}\text{H}$, and 7.51 ppm for -NCH=CHN-), aromatic proton bands at 6.92-7.74 ppm, and methyl proton signal at 2.56 ppm, respectively.^{8a,13,14a} The ratio of integrated intensities for the proton resonances of N=CH(2):ArH(6):ArH(2) + -NCH=CHN-(2) + -NCHCH(4):-NCHCH-(4):S-CH₃(6) shows 2.00:6.06:8.34:3.83:6.03 consistent with the stoichiometric ratio of sal-mdtc: 4,4'-bpe = 2:1. $^1\text{H-NMR}$ data of other complexes are given in the experimental section. The complexes of **3** and **4** show similar $^1\text{H-NMR}$ spectra to the complex **1**, except disappearing the proton resonances for the -NCH=CHN- of 4,4'-bpe and appearing the proton resonance for the phenyl amine of sal-phtsc ligand instead of disappearing the proton resonances for the methyl group of sal-mdtc ligand, respectively. The azomethine proton resonances (8.92 for **1**, 8.95 for **3**, and 8.81 ppm for **4**) in all complexes are shifted to the down field compared to the resonances (8.53 ppm for sal-mdtcH₂ and 8.49 ppm for sal-phtscH₂) of the free ligands. Also, the signals for one OH proton resonance (13.34 ppm for sal-mdtcH₂ and 11.78 ppm for sal-phtscH₂) and one NH proton (10.24 ppm for sal-mdtcH₂ and 10.05, 9.98 ppm for sal-phtscH₂) of the free schiff base ligands 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.

Structural description of compound 2. The molecular structure of complex **2** is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The dinuclear complex crystallizes in the rhombohedral space group R-3 with a crystallographic center of inversion, the two equivalent halves of the molecule have a *trans* disposition with respect to the C15=C15a at the center. The molybdenum centers have a distorted octahedral coordination environment that consists of an sal-mdtc²⁻, two terminal oxygen atoms, and one nitrogen atom of one-half of the 4,4'-bpe group. Two molybdenum atoms (Mo-Mo distance = 14.189 Å) are linked by two bridge nitrogen atoms of 4,4'-bpe. The tridentate schiff base ligand, sal-mdtc²⁻ is bonded to the *cis*-[Mo(VI)O₂]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. In general the coordination environment around molybdenum centers

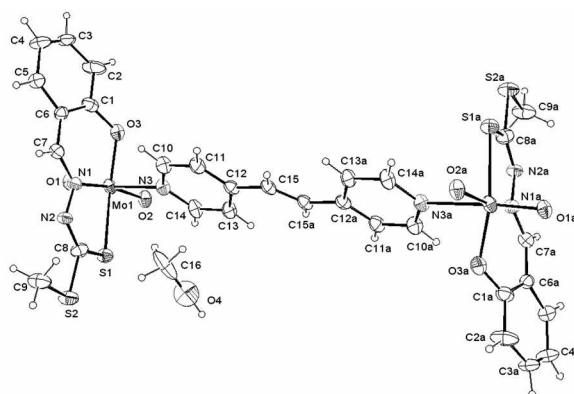


Figure 1. OrtepIII²⁵ drawing of **2**. Displacement ellipsoids are drawn at 30% probability level. Symmetry transformations used to generate equivalent atoms: #a $-x+2, -y+1, -z+1$.

resemble those of the mononuclear *cis*-dioxomolybdenum (VI) complexes with tridentate schiff base ligand have been prepared previously in our laboratory.¹²

The average Mo=O bond length (1.711(7) Å) and the O=Mo=O bond angle (106.0(3)°) are typical for *cis*- MoO_2 group.²²⁻²⁴ The Mo-O3 bond length [1.921(8) Å] is relatively longer than the values of Mo=O_(terminal) due to the bond order. The bond lengths for Mo-S1 and Mo-N1 are also similar to those reported for other complexes¹² (Table 2). The *cis*- and *trans*-L-Mo-L angles are in the range of 75.7(2)-106.4(3)° and 151.1(2)-169.6(3)°, respectively. To a large extent these distortions stem from the incorporation of Mo into a five-membered ring. The bond lengths, N1-C7 (1.285(13) Å) and N2-C8 [1.290(12) Å] indicate that these are double bonds, respectively (normal single bond is 1.364 Å).^{9b} The metric parameters for the five- and six-membered ring which are formed upon coordination of ligand are unexceptional and compare closely to those in related molecules.^{12b} The metric parameters for 4,4'-bpe are as follows: 1.34(2)-1.46(2) and *ca.* 1.35(1) Å for C-C and C-N bond lengths, and 116.7(9)-124.1(11) and 117.6(9)° for C-C-C and C-N-C angles, respectively.

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

Mo(1)-O(1)	1.707(7)	Mo(1)-O(2)	1.714(7)
Mo(1)-O(3)	1.921(8)	Mo(1)-N(1)	2.267(8)
Mo(1)-N(3)	2.426(8)	Mo(1)-S(1)	2.471(3)
S(1)-C(8)	1.719(11)	S(2)-C(8)	1.791(11)
N(2)-C(8)	1.290(12)	N(1)-N(2)	1.422(10)
N(1)-C(7)	1.285(13)	C(6)-C(7)	1.410(13)
C(1)-C(6)	1.396(14)	O(3)-C(1)	1.371(14)
N(3)-C(10)	1.353(13)		
O(2)-Mo(1)-O(1)	106.0(3)	O(2)-Mo(1)-O(3)	106.4(3)
O(1)-Mo(1)-O(3)	98.2(3)	O(2)-Mo(1)-N(1)	158.5(3)
O(1)-Mo(1)-N(1)	92.1(3)	O(3)-Mo(1)-N(1)	81.8(3)
O(2)-Mo(1)-N(3)	84.2(3)	O(1)-Mo(1)-N(3)	169.6(3)
O(3)-Mo(1)-N(3)	76.9(3)	N(1)-Mo(1)-N(3)	78.2(3)
O(2)-Mo(1)-S(1)	89.4(3)	O(1)-Mo(1)-S(1)	100.5(2)
O(3)-Mo(1)-S(1)	151.1(2)	N(1)-Mo(1)-S(1)	75.7(2)
N(3)-Mo(1)-S(1)	80.9(2)	S(1)-C(8)-S(2)	113.5(5)

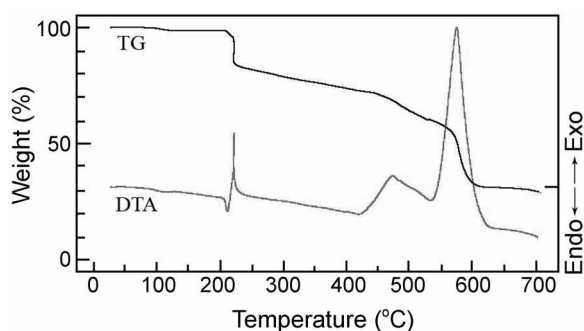


Figure 2. TG curve of complex 1.

Thermal properties. The thermogravimetric analyses (TGA) of complexes were conducted in the temperature range of 30–700 °C with a 10 °C/min temperature interval. Their thermal decomposition behaviors are very similar to each other. No obvious decompositions are observed below 200 °C. Above this temperature the TG curve exhibits two steps of weight losses. The TG curve for the representative complex 1 is shown in Figure 2.

Complex 1 undergoes a rapid weight loss of 16.18% in the temperature range of 200–242 °C, corresponding to the release of 4,4'-bpe ligand (calculated: 17.48%). The second gradual weight loss of 50.81% in the range of 242–613 °C due to the loss of two sal-mdtc ligands in the formula unit (calculated: 50.59%) is observed. These weight losses were accompanied by exothermic effect on the DTA curve with maximum at 220, 472, and 593 °C, respectively. For complex 3, the TGA curve shows a rapid and significant weight loss of 30.91% in the temperature ranges of 210–253 °C and the gradual weight loss of 36.27% between 253 and 543 °C. The total weight loss of 67.18% may be the concomitant release of the 4,4'-bpy and sal-mdtc ligands, with a calculated value of 70.27%. The complex 4 shows the decompositions of 4,4'-dpdo and sal-phpsc ligand in the temperature range of 220–242 °C with weight loss of 20.22% (calculated 19.15%) and of 242–568 °C with weight loss of 51.99% (calculated 54.81%), respectively.

Conclusions

Four new dimeric dioxomolybdenum(VI) complexes, $[\text{Mo}_2\text{O}_4(\text{schiff base})_2(\text{diamine})]$ type, with the ONS-donor schiff base and diamine ligands or its derivatives have been synthesized and characterized. In all complexes, the structure consists of two $[\text{MoO}_2(\text{schiff base})]$ moieties bridged by two N atoms from diamine ligand. To our knowledge, these structures are not common. It is anticipated that the various structure of multinuclear molybdenum complexes may be synthesized under the different reaction conditions, such as stoichiometry, solvent effect, and etc.

Supporting information available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-689421 (2)). 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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