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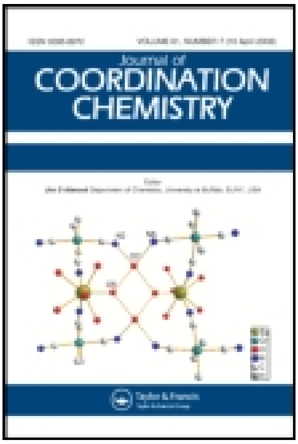

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Synthesis, chemical, electrochemical, and structural characterization of binuclear dioxo-bridged molybdenum(VI) complexes of tridentate ONS donors

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Synthesis, chemical, electrochemical, and structural characterization of binuclear dioxo-bridged molybdenum(VI) complexes of tridentate ONS donors

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A number of dioxo-bridged binuclear molybdenum(VI) complexes with diprotic tridentate ONS donor Schiff bases (H_2L^1, H_2L^2, H_2L^3, and H_2L^4) obtained by the condensation of salicylaldehyde/2-hydroxyacetophenone with S-benzyl and S-methyl dithiocarbazates have been synthesized using the Mo(V) complex $(NH_4)_2[Mo^VOCl_5]$ as starting material. All these reactions are carried out in air and the Mo^VO center of the precursor complex undergoes spontaneous aerial oxidation leading to the formation and isolation of molybdenum(VI) complexes $Mo_2O_4L_2$. The complexes were characterized by elemental analyses, various spectroscopic techniques (UV-Vis, infrared etc.), magnetic susceptibility at room temperature, molar conductivity, and cyclic voltammetry. One of the complexes, $Mo_2O_4L_2{}^1$ (**1**), was structurally characterized by single-crystal X-ray crystallography.

Keywords: Dioxo-bridged binuclear molybdenum(VI) complexes; Dithiocarbazate; Schiff bases; X-ray crystal structure

1. Introduction

The chemistry of Mo(VI) has received special attention because of its relevance to several biological [1, 2] and industrial [3–5] processes. Dioxomolybdenum complexes exhibit oxo-transfer ability to selected substrates and mimic the active centers of some oxo-transfer molybdoenzymes [6a]. This bioinorganic aspect of such complexes resulted in studies of a large number of mononuclear $Mo^{VI}O_2L$ complexes with ONO and ONS donors. However, compared to mononuclear complexes, binuclear dioxo-bridged complexes have not been studied adequately [6b–d]. This work reports the synthesis of four $Mo_2O_4L_{2-}$ dioxo-bridged complexes of tridentate ONS chelating ligands using a Mo(V) precursor $(NH_4)_2[Mo^VOCl_5]$. Characterizations by elemental analyses and various spectroscopic [infrared (IR), UV-Vis] methods are also reported.

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One of these complexes ($Mo_2O_4L_2^1$) has been structurally characterized by single-crystal X-ray crystallography. The chemical activity and electrochemical behavior of these complexes have been examined. Simultaneous oxo-transfer and bridge splitting of the dinuclear complexes have been established by the isolation of $Mo^{IV}OL$ complexes, which could be easily oxidized to the corresponding mononuclear $Mo^{VI}O_2L$ species that are obtained in the solid state. These dioxo-bridged binuclear complexes could not be prepared directly from a $Mo^{VI}O_2^{2+}$-containing precursor like $MoO_2(acac)_2$/Na-molybdate/NH_4-molybdate. No other report on the synthesis of such Mo(VI) complexes starting from a Mo(V) complex has appeared.

2. Experimental

2.1. *Materials*

$(NH_4)_2[MoOCl_5]$ was prepared as described [7]. Reagent grade solvents were dried and distilled prior to use. All other chemicals used for preparative work were of reagent grade, available commercially, and used without purification.

2.2. *Synthesis*

2.2.1. Synthesis of the ligands H_2L^1, H_2L^2, H_2L^3, and H_2L^4. The Schiff bases H_2L^1, H_2L^2 and H_2L^3, H_2L^4 were prepared by condensing S-benzyl and S-methyl dithiocarbazates with salicylaldehyde and 2-hydroxyacetophenone in ethanol (scheme 1). The ligands were satisfactorily characterized by elemental analyses, IR, and ^1H NMR [8, 9].

2.2.2. Synthesis of complexes. $Mo_2O_4L_2^1$ (1). To a filtered solution of 0.325 g (1.0 mmol) of $(NH_4)_2[MoOCl_5]$ in 20 mL dry methanol, 0.302 g (1.0 mmol) of H_2L^1 in 15 mL of dry methanol was added. The reddish brown solution was stirred at room temperature in open air for 4 h. The reddish brown compound that separated was filtered, washed with cold methanol, and dried *in vacuo* over anhydrous $CaCl_2$. Yield ~75%. Anal. Calcd for $C_{30}H_{24}N_4S_4O_6Mo_2$ (%): C, 42.05; H, 2.80; N, 6.54; Mo, 22.43. Found (%): C, 42.16; H, 2.68; N, 6.49; Mo, 23.00. IR (KBr pellet), cm^{-1}: $\nu_{(C=N)}$ 1599(s), $\nu_{(Mo=O)}$ 947(s), 918(m), $\nu_{(Mo-O-Mo)}$ 752(s), $\nu_{(Mo-S)}$ 393(m), $\nu_{(Mo-N)}$ 570(s); UV-Vis (CH_2Cl_2) [λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$)]: 276 (5750), 311 (5660), 398 (2421).

Complexes $Mo_2O_4L_2$ (**2**), $Mo_2O_4L_2$ (**3**), $Mo_2O_4L_2$ (**4**) were prepared similarly using 0.226 g (1.0 mmol) of H_2L^2, 0.316 g (1.0 mmol) of H_2L^3, and 0.24 g (1.0 mmol) of H_2L^4, respectively, with yields of 70–75%.

$Mo_2O_4L_2^2$ (2). Anal. Calcd for $C_{18}H_{16}N_4S_4O_6Mo_2$ (%): C, 30.68; H, 2.27; N, 7.95; Mo, 27.27. Found (%): C, 30.24; H, 2.32; N, 7.93; Mo, 27.32. IR (KBr pellet), cm^{-1}: $\nu_{(C=N)}$ 1599(s), $\nu_{(Mo=O)}$ 961(vs), 909(m), $\nu_{(Mo-O-Mo)}$ 758(s), $\nu_{(Mo-S)}$ 320(m), $\nu_{(Mo-N)}$ 546(s); UV-Vis (CH_2Cl_2) [λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$)]: 236 (5334), 309 (2522), 341 (1982), 412 (1895), 464 (2107).

Keto (thione) form

Enol (thiol) form

R	R1	Ligand
CH_2Ph	H	H_2L^1
Me	H	H_2L^2
CH_2Ph	Me	H_2L^3
Me	Me	H_2L^4

Scheme 1. Tautomeric thione and thiol forms of the Schiff bases.

$Mo_2O_4L_2^3$ (3). Anal. Calcd for $C_{32}H_{28}N_4S_4O_6Mo_2$ (%): C, 43.44; H, 3.17; N, 6.33; Mo, 21.72. Found (%): C, 43.13; H, 3.00; N, 6.41; Mo, 22.21. IR (KBr pellet), cm^{-1}: $\nu_{(C=N)}$ 15995(s), $\nu_{(Mo=O)}$ 989(s), 971(s), $\nu_{(Mo–O–Mo)}$ 756(s), $\nu_{(Mo–S)}$ 325(m), $\nu_{(Mo–N)}$ 630(m); UV-Vis (CH_2Cl_2) [λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$)]: 300 (10,271), 346 (8217), 469 (2167).

$Mo_2O_4L_2^4$ (4). Anal. Calcd for $C_{20}H_{20}N_4S_4O_6Mo_2$ (%): C, 32.78; H, 2.73; N, 7.65; Mo, 26.22. Found (%): C, 33.00; H, 2.52; N, 7.35; Mo, 25.96. IR (KBr pellet), cm^{-1}: $\nu_{(C=N)}$ 1595(s), $\nu_{(Mo=O)}$ 1003(m), 966(s), $\nu_{(Mo–O–Mo)}$ 757(s), $\nu_{(Mo–S)}$ 360(m), $\nu_{(Mo–N)}$ 625(m); UV-Vis (CH_2Cl_2) [λ_{max}/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$)]: 272 (7341), 295 (7497), 379 (3635), 468 (2239).

All four complexes are diamagnetic.

2.3. *Physical measurements*

Elemental analyses were performed on a Perkin-Elmer 240 C, H, N analyzer. IR spectra were recorded as KBr pellets on a Perkin-Elmer model 883 IR spectrophotometer. Electronic spectra were recorded on a HITACHI U-3501 UV-Vis recording spectrophotometer. Magnetic susceptibilities were measured with a PAR model 155 vibrating sample magnetometer with $Hg[Co(SCN)_4]$ as calibrant. Electrochemical data were collected on a Sycopel model AEW2 1820 F/S instrument at 298 K using a Pt working electrode, a Pt auxiliary electrode, and a SCE reference electrode. Cyclic voltammograms were recorded in DMF containing 0.1 mol L^{-1} TEAP as supporting electrolyte.

Table 1. Crystallographic data for **1**.

	1
Chemical formula	$C_{30}H_{24}Mo_2N_4O_6S_4$
Formula weight (M)	856.65
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	28.443(3)
b	7.3623(10)
c	16.2441(15)
β	93.100(8)
Volume (Å^3), *Z*	3396.6(7), 4
Calculated density (g cm^{-3})	1.675
Absorption coefficient (Mo-Kα) (mm^{-1})	1.032
F (000)	1712
Goodness of fit on F^2	1.035
Final *R* indices ($I > 2\sigma$(I))	$R_1 = 0.0402$, $wR_2 = 0.1040$
R indices (all data)	$R_1 = 0.0518$, $wR_2 = 0.1104$
Largest difference peak and hole (e Å^{-3})	0.852 and −1.301

2.4. *Crystallographic measurements*

The crystallographic data for **1** were collected on a Bruker P4 diffractometer equipped with graphite-monochromated Mo-Kα ($\lambda = 0.71013$ Å) radiation using ω-scans. The crystal structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares based on F^2 with anisotropic displacement parameters of non-hydrogen atoms using SHELXL-97. The hydrogens were included in calculated positions. The crystallographic data and structure refinement parameters for **1** are given in table 1.

3. Results and discussion

3.1. *Syntheses*

In our initial attempt to prepare dioxo-bridged Mo(VI) complexes of the ONS donor ligands used in this work, we tried $MoO_2(acac)_2$ as well as Na- and NH_4-molybdates as the source of Mo(VI) but could not isolate the desired products. From our previous experience (unpublished results) when $(NH_4)_2[MoOCl_5]$ was used as the molybdenum source and the reactions were performed in open air, the Mo(V) center underwent oxidation and formation of dioxo-bridged Mo(VI) complexes which could be isolated as solids. For this reason $(NH_4)_2[MoOCl_5]$ was used as molybdenum source in the present study.

Reddish brown dioxo-bridged binuclear Mo(VI) complexes $[Mo_2O_4L_2]$ (**1**–**4**) were prepared by stirring filtered solutions of $(NH_4)_2[MoOCl_5]$ in methanol with the appropriate ligand in 1 : 1 molar ratio at room temperature in open air. Yield ~70–75%. Oxidation of the monooxo Mo(V) center of the starting material occurs spontaneously during the stirring of the reaction mixture, resulting in the isolation of dioxo-bridged Mo(VI) complexes, $Mo_2O_4L_2$. As monomeric $Mo^{VI}O_2L$ complexes could not be prepared by this method, a two-step indirect way was utilized. $Mo^{IV}OL$ complexes were obtained by simultaneous bridge-splitting and oxo-abstraction of the binuclear $Mo_2O_4L_2$ species using PPh_3 followed by oxo-insertion using pyridine N-oxide/DMSO.

The binuclear molybdenum(VI) complexes have been characterized on the basis of elemental analyses and other analytical data including solution conductance and magnetic susceptibility measurements. All the compounds are air stable in the solid state and are readily soluble in alcohol, CH_2Cl_2, CH_3CN, DMF, and DMSO, but insoluble in water. The complexes are diamagnetic at room temperature as expected for a d^0 Mo(VI) [10]. Molar conductivity data in $10^{-3}\,mol\,L^{-1}$ CH_2Cl_2 indicate that they are non-electrolytes. All the Mo(VI) complexes (both bi and mononuclear) are satisfactorily characterized by IR, electronic spectra, and cyclic voltammetric data. Complex **1** has been structurally characterized by single-crystal X-ray diffraction.

3.2. *Spectral characteristics*

Characteristic IR bands of binuclear molybdenum(VI) complexes are listed in the experimental section. A strong $\nu(C{=}N)$ [11, 12] was observed at 1595–1599 cm^{-1} for all the complexes. New bands at 570–660 cm^{-1} for the complexes are assigned to ν(Mo–N) [13, 14]. The complexes exhibit a medium intensity band at 320–393 cm^{-1} assigned to ν(Mo–S) [15]. Two IR bands are observed in the 1003–909 cm^{-1} region, the higher frequency band from the anti-symmetric and the lower frequency band from the symmetric stretching mode of $[MoO_2]^{2+}$ [13, 16, 17a]. A strong band at 755 cm^{-1} for all the complexes may be assigned to ν(Mo–O–Mo) [17b].

Electronic spectra of the binuclear molybdenum(VI) complexes were recorded in dry dichloromethane (data in Section 2). $Mo_2O_4L_2$ exhibit several bands from 469–236 nm. The absorption maxima located in the 400–300 nm range may be assigned to $S(p\pi)$–$Mo(d\pi)$ LMCT transition caused by the promotion of an electron from the filled HOMO of the ligand of primarily sulfur $p\pi$ character to the empty LUMO of molybdenum $d\pi$ [18]. Other LMCT bands are observed at 300–270 nm [12, 19–21]. Bands below 270 nm are due to intraligand transitions.

3.3. *Electrochemistry*

Cyclic voltammograms of binuclear molybdenum(VI) complexes (**1**–**4**) at a platinum electrode were recorded in dry degassed DMF containing 0.1 $mol\,L^{-1}$ TEAP as the supporting electrolyte over a potential range of 0.0 to −1.5 V. Results are presented in table 2 and a representative diagram is shown in figure 1. Each complex (**1**–**4**) exhibits only one irreversible two electron, one-step reduction within the potential window scanned (*vs*. SCE), assigned to Mo^{VI}–Mo^{VI}/Mo^{V}–Mo^{V} process [12, 19, 20]. The expected Mo^{V}–Mo^{V} to Mo^{IV}–Mo^{IV} step could not be observed, probably because of the rapid decomposition of the very unstable Mo^{V}–Mo^{V} species.

Table 2. Cyclic voltammetric results[a] (V *vs*. SCE) for $[Mo_2O_4L_2]$ at 298 K.

Complexes	E_{pc} (V)
$Mo_2O_4L^1_2$ (**1**)	−0.99
$Mo_2O_4L^2_2$ (**2**)	−1.00
$Mo_2O_4L^3_2$ (**3**)	−1.02
$Mo_2O_4L^4_2$ (**4**)	−1.03

[a] Solvent: DMF (dry, degassed); supporting electrolyte: 0.1 mol L^{-1} TEAP; solution strength: 10^{-3} mol L^{-1}; working electrode: platinum; reference electrode: SCE; 50 m Vs^{-1}.

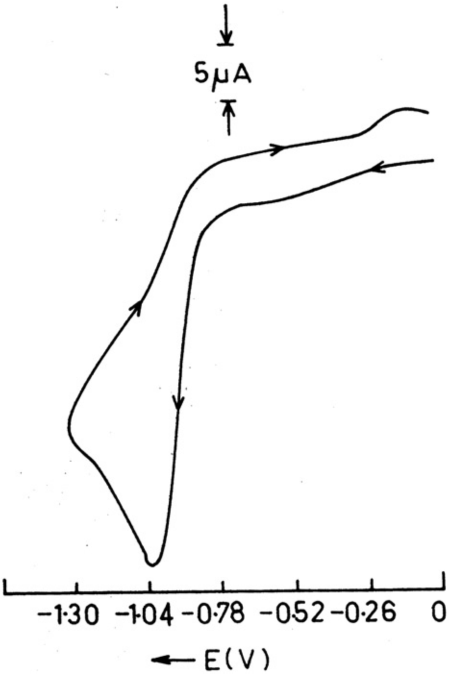

Figure 1. Cyclic voltammogram of $Mo_2O_4L_2{}^4$ (**4**) in DMF at 298 K.

3.4. *Description of crystal structure of $Mo_2O_4L^1_2$ (1)*

The reddish brown binuclear complex $[Mo_2O_4L^1_2]$ (**1**) crystallized in the monoclinic space group *C2/c* and two halves of **1** are crystallographically equivalent with closely matching structural dimensions. The molecular structure and the atom labeling of **1** are shown in figure 2. Crystallographic data for **1** are presented in table 1 and selected bond lengths and angles are presented in tables 3 and 4, respectively. Structure of one half of the complex is described in detail. The two oxo's of one $[MoO_2]^{2+}$, ONS donors of H_2L^1, and one oxygen of another $[MoO_2]^{2+}$ complete the distorted octahedral coordination around Mo^{VI}. O(1), N(1), S(1) from the ligand and one terminal oxygen O(3)* occupy the meridonial plane [22, 23] forming one

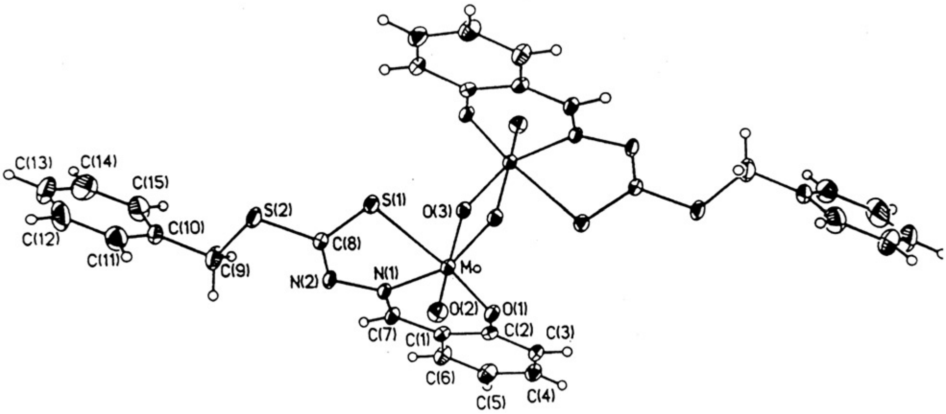

Figure 2. An ORTEP diagram (30% probability) and atom-numbering scheme of $Mo_2O_4L_2{}^1$ (**1**).

Table 3. Selected bond lengths (Å) for **1**.

Mo–O(1)	1.911(2)	N(1)–C(7)	1.305(4)
Mo–O(2)	1.687(2)	N(2)–C(8)	1.289(5)
Mo–O(3)	2.465(2)	N(1)–N(2)	1.412(4)
Mo–N(1)	2.22(2)	S(1)–C(8)	1.743(4)
Mo–S(1)	1.414(9)	C(1)–C(2)	1.402(4)
O(1)–C(2)	1.343(4)	C(1)–C(7)	1.430(4)

Table 4. Selected bond angles (°) for **1**.

O(1)–Mo–O(2)	99.92(12)	O(2)–Mo–N(1)	102.97(12)
O(1)–Mo–O(3)	77.89(9)	O(2)–Mo–S(1)	97.64(9)
O(1)–Mo–O(3)*	103.51(10)	O(3)–Mo–N(1)	76.64(9)
O(1)–Mo–N(1)	81.87(10)	O(3)*–Mo–N(1)	149.09(10)
O(1)–Mo–S(1)	154.06(8)	O(3)–Mo–S(1)	84.37(6)
O(2)–Mo–O(3)	177.80(11)	N(1)–Mo–S(1)	75.67(7)
O(2)–Mo–O(3)*	105.92(12)	–	–

*Symmetry transformation $1-x$, $-y+3$, $-z+1$.

five-membered and another six-membered chelating ring around $[MoO_2]^{2+}$ with bite angles [N(1)–Mo–S(1) and N(1)–Mo–O(1)] 75.67(7)° and 81.87(10)°, respectively. The other oxo-oxygen O(2) occupies one apical position while the other apical position is occupied by the oxo-oxygen O(3) of the dioxo bridge. The Mo–O(3) bond [2.465(2) Å] is much longer than the Mo–O(3)* bond [1.742(2) Å], indicating that the oxo-oxygen O(3) of the other $[Mo^*O_2]^{2+}$ moiety is weakly bonded to $[MoO_2]^{2+}$ and vice versa. As the ligand coordinates through the thiolate sulfur, the C(8)–S(1) bond assumes single bond character but in **1** this length is 1.743(4) Å, between the length of the C–S and the C=S bond and may be attributed to electron delocalization in the coordinated ligand [24, 25]. The adjacent C(8)–N(2) bond length is 1.289(5) Å, closer to C=N than normal C–N distance. The N(1)–N(2) bond distance of 1.412(4) Å reveals predominant single bond character.

3.5. *Study of reactivity*

On simultaneous dioxo-bridge splitting and oxo-abstraction, the binuclear dioxo Mo(VI) complexes form mononuclear monooxo Mo(IV) complexes MoOL (yield ~75–80%) when reacted with PPh_3 in 1 : 3 molar proportions in dry CH_3OH/CH_3CN. The oxo-transfer reaction may be represented as

$$Mo_2O_4L_2 + 2PPh_3 \xrightarrow{CH_3CN} 2MoOL + 2OPPh_3$$

When these MoOL complexes in CH_3CN are reacted with excess DMSO or pyridine N-oxide, brown color of the solution gradually changed to orange indicating oxo-transfer from DMSO/pyridine N-oxide to the mono oxo $[MoO]^{2+}$ center generating mononuclear MoO_2L type complexes, isolated (yield ~60%) and characterized. This two-step process is a new method of obtaining mononuclear Mo(VI) complexes from binuclear dioxo-bridged $Mo_2O_4L_2$ species.

$$MoOL + DMSO/Pyridine\text{-}N\text{-}oxide \xrightarrow{CH_3CN} MoO_2L + Me_2S/pyridine.$$

4. Conclusion

This work reports the synthesis and characterization of four dioxo-bridged Mo(VI) complexes starting from the Mo(V) compound $(NH_4)_2[MoOCl_5]$ along with the structural characterization of one representative member. During the process of preparation Mo(V) undergoes spontaneous aerial oxidation and dioxo-bridge formation. Cyclic voltammetric responses are explored. Chemical reactivity toward oxo-abstracting reagents like PPh_3 followed by oxo-insertion by pyridine N-oxide/DMSO led to the isolation of mononuclear MoO_2L complexes. Thus a new method of obtaining mononuclear MoO_2L complexes starting from the corresponding binuclear dioxo-bridged Mo(VI) complexes has been achieved.

Supplementary material

Crystallographic data have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-366033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) and are available on request quoting the deposition number 159189 for **1**.

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