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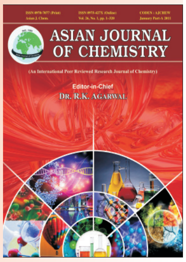

Synthesis, Characterization and Crystal Structure of Acetohydroxamate-Coordinated Molybdenum(VI) Complex Derived from 2-[(2-Ethylaminoethylimino)methyl]-4-methoxyphenol

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Reaction of $[MoO_2(acac)_2]$ (where acac = acetylacetonate) with 2-[(2-ethylaminoethylimino)methyl]-4-methoxyphenol (L) and acetohydroxamic acid (H_2AHA) in methanol yielded a new mononuclear molybdenum(VI) complex, $[MoO_2L(AHA)]$. Crystal and molecular structure of the complex were determined by single crystal X-ray diffraction method. The complex was further characterized by IR and elemental analysis and thermogravimetric analysis. Single crystal X-ray structural studies indicate that the zwitterionic Schiff base ligand L coordinates to the MoO_2 core through the phenolate oxygen and azomethine nitrogen and the dianionic AHA ligand coordinates to the MoO_2 core through the two oxygen atoms. The Mo atom in the complex is in octahedral coordination. Crystal structure of the complex is stabilized by intermolecular N-H···N and C-H···O hydrogen bonds, as well as π···π interactions.

Keywords: Schiff base ligand, Acetohydroxamate ligand, Molybdenum complex, Crystal structure, Thermal property.

INTRODUCTION

The coordination chemistry of molybdenum(VI) has attracted considerable attention due to its recently discovered biochemical significance[1-3] as well as for the efficient catalytic properties in several organic synthesis procedures[4-7]. In recent years, a good number of molybdenum(VI) complexes with Schiff bases derived from salicylaldehyde and primary amines have been reported[8-10]. Usually, the Schiff bases coordinate to the octahedral coordination Mo atoms through two or three donor atoms, with the other positions occupied by oxo oxygen groups and secondary ligands, such as methanol, ethanol, DMF, DMSO, water, *etc*[8-13]. Acetohydroxamic acid (H_2AHA) is a bidentate ligand in coordination chemistry[14-17]. Lin and co-workers have reported a AHA-coordinated molybdenum(VI) complex[18]. However, no AHA-coordinated molybdenum complexes with Schiff bases have seldom been reported so far. In the present work, we report the synthesis, characterization and crystal structure of a new AHA-coordinated dioxomolybdenum(VI) complex derived from the Schiff base 2-[(2-ethylaminoethylimino)methyl]-4-methoxyphenol (L). Thermal stability of the complexes was also investigated.

EXPERIMENTAL

Commercially available 5-methoxysalicylaldehyde and *N*-ethylethane-1,2-diamine were purchased from Sigma-Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H and N elemental analyses were performed with a Perkin-Elmer elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000-400 cm^{-1} region. Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TGA-DTA thermal analyses system.

Synthesis of the complex: 5-Methoxysalicylaldehyde (1 mmol, 0.15 g) and *N*-ethylethane-1,2-diamine (1 mmol, 0.09 g) were mixed in methanol (20 mL). The mixture was stirred at room temperature for 0.5 h to give a yellow solution. To the solution was further added a methanolic solution (10 mL) of acetohydroxamic acid (1 mmol, 0.075 g) and a methanolic solution (10 mL) of $[MoO_2(acac)_2]$ (1 mmol, 0.33 g). The final mixture was further stirred at room temperature for 0.5 h to give a yellow solution. The resulting solution was allowed to stand in air for a few days. Yellow block-shaped crystals suitable for X-ray single crystal diffraction were formed at the bottom of the vessel. The isolated products were washed three times with cold methanol and dried in air. Yield: 36 %; Anal. Calcd. for $C_{14}H_{21}N_3O_6Mo$: C, 39.7; H, 5.0; N, 9.9. Found: C, 39.9; H, 5.1; N, 9.8.

X-ray crystallography: Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the

SAINT program[19], and multi-scan absorption corrections were performed using the SADABS program[20]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL[21]. All of the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data are listed in Table-1. Selected bond lengths and angles are given in Table-2.

TABLE-1
CRYSTALLOGRAPHIC AND EXPERIMENTAL
DATA FOR THE COMPLEX

m.f.	$C_{14}H_{21}MoN_3O_6$
m.w.	423.3
T (K)	298(2)
Crystal shape/color	Block/yellow
Crystal size (mm^3)	0.20 × 0.18 × 0.17
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.408(1)
b (Å)	12.534(1)
c (Å)	14.695(2)
α (°)	90
β (°)	101.558(3)
γ (°)	90
V (Å^3)	1697.7(3)
Z	4
D_c (g cm^{-3})	1.656
μ(Mo-K_α) (mm^{-1})	0.808
F(000)	864
h, k, l ranges	-11, 11; -15, 15; -18, 17
Measured reflections	17324
Independent reflections	3442
Observed reflections (I ≥ 2σI))	3313
Min. and max. transmission	0.8551 and 0.8749
Parameters	220
Restraints	0
Goodness-of-fit on F^2	1.123
R_1, wR_2 [I ≥ 2σI)][a]	0.0213, 0.0535
R_1, wR_2 (all data)[a]	0.0223, 0.0543
Largest peak and deepest hole (e Å^{-3})	0.341, -0.375

[a] $R_1 = F_o\text{-}_c/F_o$, $wR_2 = [\sum w(F_o^2\text{-}c^2)/\sum w(F_o^2)^2]^{1/2}$

TABLE-2
SELECTED BOND DISTANCES (Å) AND
ANGLES (°) FOR THE COMPLEX

Bond lengths,	Å	Bond lengths,	Å
Mo1-O1	1.9506(12)	Mo1-O3	2.1091(12)
Mo1-O4	1.9551(12)	Mo1-O5	1.6999(13)
Mo1-N1	2.4284(14)	Mo1-O6	1.7373(12)
Bond angles	(°)	Bond angles	(°)
O6-Mo1-O4	92.94(6)	O1-Mo1-O4	152.64(5)
O6-Mo1-O1	103.79(6)	O5-Mo1-O4	102.34(6)
O5-Mo1-O6	103.73(6)	O5-Mo1-O1	94.62(6)
O5-Mo1-O3	97.46(6)	O6-Mo1-O3	157.25(5)
O1-Mo1-O3	82.39(5)	O4-Mo1-O3	74.31(5)
O5-Mo1-N1	172.19(6)	O6-Mo1-N1	82.20(5)
O1-Mo1-N1	78.89(5)	O4-Mo1-N1	82.20(5)
O3-Mo1-N1	77.52(5)	-	-

RESULTS AND DISCUSSION

Replacement of two acetylacetonate ligands in $[MoO_2(acac)_2]$ by Schiff base and acetohydroxamate ligands resulted in the formation of mononuclear molybdenum(VI) oxo complex. The zwitterionic Schiff base ligand coordinates to the *cis*-MoO_2 core *via* the phenolate-oxygen and imino-nitrogen. The dianionic AHA ligand coordinates to the *cis*-MoO_2 core *via* two oxygen atoms. The complex is soluble in methanol, ethanol and acetonitrile. The molar conductance of the complex at the concentration of 10^{-4} M in methanol is27 Ω^{-1} cm^2 mol^{-1}, indicating the non-electrolyte nature in this solution[22].

Crystal structure description of the complex: The molecular structure and atom numbering scheme of the complex is shown in Fig. 1. The zwitterionic Schiff base ligand behaves in a bidentate manner in which the phenolate O and imino N atoms coordinate to the *cis*-MoO_2 core. The dianionic AHA ligand coordinates to the *cis*-MoO_2 core through enolate O and hydroxy O atoms, forming one five-membered chelate ring. The coordination geometry around the Mo atom is highly distorted octahedral. The equatorial plane is defined by two donor atoms (O3 and O4) of the AHA ligand, the O1 atom of the Schiff base ligand and one oxo group (O6). The two axial positions are occupied by the N1 atom of the Schiff base ligand the other oxo group (O5). The Mo1-N1 and Mo1-O3 bonds are significantly longer than the other bonds, which is caused by the *trans* effects of the oxo groups. The atoms O1, O3, O4 and O6 in the complex show high degree of planarity from the equatorial plane; the Mo atom deviates from the plane by 0.321(1) Å in the direction of O5 oxo group. The distances between atoms Mo1 and O5 or O6 are in the range 1.70-1.74 Å, indicating they are typical Mo=O double bonds. The Mo=O, Mo-O and Mo-N bonds in the complex are similar to those observed in the literature[8-13]. The angular distortion in the octahedral environment around Mo mainly comes from the five- and six-membered chelate rings taken by the ligands. For the same reason, the *trans* and *cis* angles are significantly deviate from the ideal values of 180° and 90°, respectively.

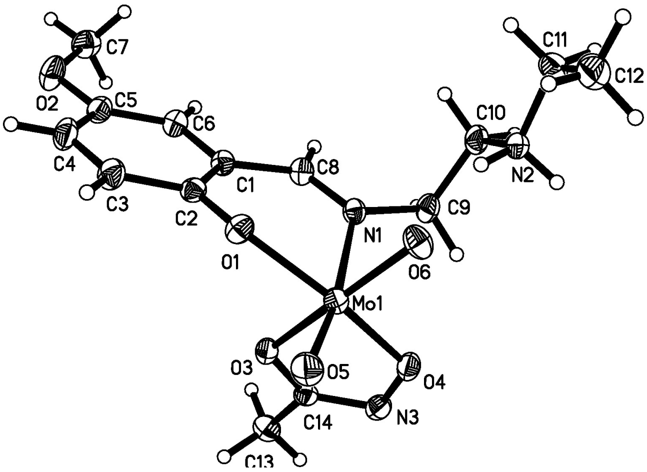

Fig. 1. ORTEP plot of the molecular structure of the complex. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level

In the crystal structure of the complex, molecules are linked through intermolecular hydrogen bonds (Table-3) and weak π···π interactions (Table-4), to form 3D network (Fig. 2).

IR spectra: The complex exhibits two bands at 837 and 917 cm^{-1}, assigned to symmetric and asymmetric vibrations of the *cis*-MoO_2 core, respectively. The intense ν(C=N) absorption

TABLE-4
PARAMETERS BETWEEN THE PLANES OF THE COMPLEX

Cg	Distance between ring centroids (Å)	Dihedral angle (°)	Perpendicular distance of Cg(I) on Cg(J) (Å)	Perpendicular distance of Cg(J) on Cg(I) (Å)
Cg1-Cg1^{iv}	4.778	0	-3.372	-3.372
Cg2-Cg2^{v}	4.125	0	3.508	3.508

Symmetry codes: (iv): -x, 1 -y, -z; (v): 1-x, 1-y, 1-z. Cg1 and Cg2 are the centroids of Mo1-O3-C14-N3-O4 and C1-C6, respectively

TABLE-3
HYDROGEN BOND DISTANCES (Å) AND
BOND ANGLES (°) FOR THE COMPLEX

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(D-H···A)
N2-H2A···N3^{i}	0.90	1.92	2.809(2)	169
N2-H2B···O6	0.90	1.89	2.752(2)	160
C8-H8···O6^{ii}	0.93	2.47	3.269(2)	144
C11-H11A···O3^{iii}	0.97	2.42	3.367(2)	164

Symmetry codes: (i) 1-*x*, 3/2 + *y*, ½-*z*; (ii) 1-*x*, -*y*, -*z*; (iii) 1 + *x*, *y*, *z*

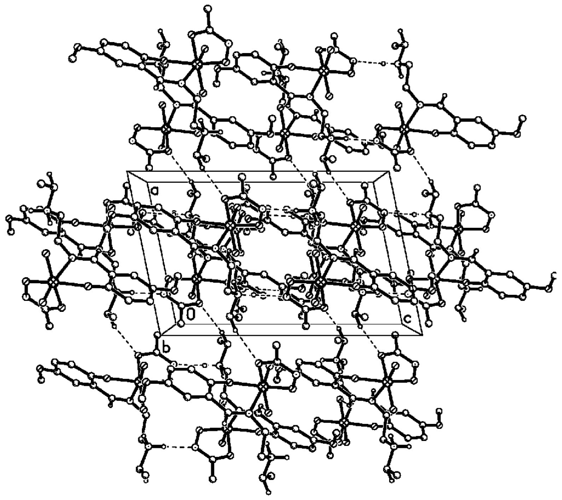

Fig. 2. Molecular packing structure of the complex, viewed along the b-axis direction. Hydrogen bonds are drawn as dashed lines

of the Schiff base ligand is observed at 1636 cm^{-1}. The medium ν(C-O) absorption of the AHA ligand is observed at 1610 cm^{-1}. The weak peaks in the low wave numbers in the region (550-400) cm^{-1} may be assigned to the vibrations of the Mo-O and Mo-N bonds in the complex.

Thermal properties: Differential thermal and thermal gravimetric analyses were conducted to examine the stability of the complex under air atmosphere and with standard corundum crucible sample holder (Fig. 3). The rate of the gas flow is 20 cm^3 min^{-1}. The heating rate is 10 °C min^{-1}. There are in general three steps of decomposition. First, from 158 to 223 °C, there corresponds to the loss of the AHA ligand. The weight loss of 17.3 % agrees well with the calculated value of 17.2 %. Second, from 223 to 610 °C, there corresponds to the loss of the Schiff base ligand and the formation of Mo_2O_3. The weight loss of 53.8 % agrees well with the calculated value of 54.5 %. The last step, from 700 to 900 °C, there corresponds to the loss of Mo_2O_3.

Supporting information: CCDC 992087 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

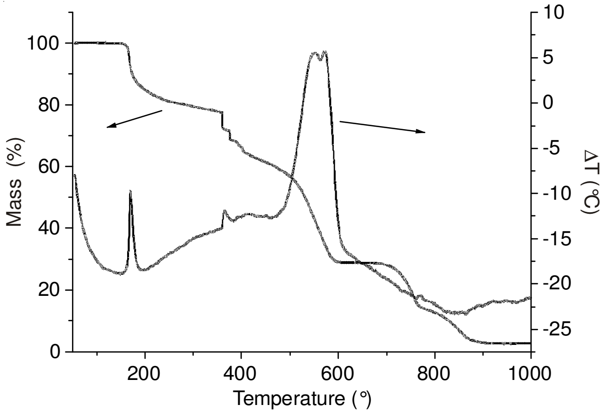

Fig. 3. DTA-TGA curves of the complex

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