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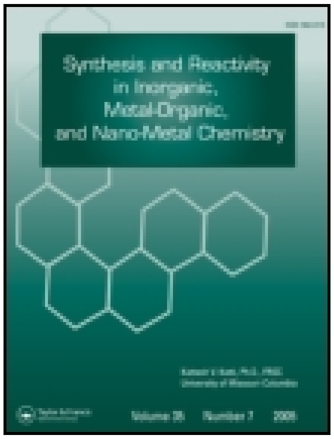

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

A Novel Aggregation of (4-Nitrophenoxy)acetic Acid [1-(2-Hydroxyphenyl)methylidene]hydrazide and Its Dioxomolybdenum(VI) Complex: Synthesis and Structure

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Accepted author version posted online: 13 May 2013.Published online: 25 Aug 2013.

To cite this article: Xiao-Qiang He (2013) A Novel Aggregation of (4-Nitrophenoxy)acetic Acid [1-(2-Hydroxyphenyl)methylidene]hydrazide and Its Dioxomolybdenum(VI) Complex: Synthesis and Structure, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:10, 1402-1405, DOI: 10.1080/15533174.2012.762676

To link to this article: http://dx.doi.org/10.1080/15533174.2012.762676

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:1402–1405, 2013

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.762676

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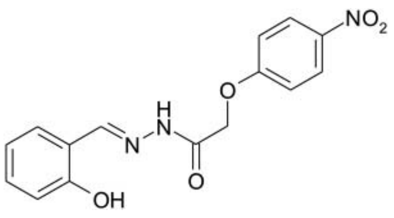
A novel aggregation of (4-nitrophenoxy)acetic acid [1-(2-hydroxyphenyl)methylidene]hydrazide and its dioxomolybdenum(VI) complex has been prepared by the reaction of salicylaldehyde, (4-nitrophenoxy)acetic acid hydrazide, and $MoO_2(acac)_2$ in methanol. The compound was characterized by elemental analysis and single-crystal X-ray diffraction method. The asymmetric unit of the compound contains a free hydrazone molecule and a dioxomolybdenum(VI) complex molecule. The Mo atom in the complex molecule is coordinated by one phenolate O, one imino N, and one enolic O atoms of the hydrazone ligand, two oxo O atoms, and one water O atom, forming an octahedral coordination.

Keywords crystal structure, hydrazone, hydrogen bonding, molybdenum complex, synthesis

INTRODUCTION

Hydrazone compounds derived from the reaction of carbonyl-containing compounds with hydrazides have attracted much attention for their effective biological activities[1–3] and interesting coordinate capabilities.[4–7] In the last few years, a large number of complexes of copper, vanadium, molybdenum, palladium, zinc, nickel, cobalt, ruthenium, organic tin, rhodium, cadmium, manganese, uranium, and germanium with hydrazone ligands have been reported,[8–16] among which there are 40 molybdenum complexes. Some of the molybdenum complexes have been reported to have versatile catalytic properties.[17–19] The construction of novel structures of molybdenum complexes with hydrazone ligands is important for the exploration of new functional materials. In the present paper, the synthesis and structure of a novel aggregation (Scheme 1) of (4-nitrophenoxy)acetic acid [1-(2-hydroxyphenyl)methylidene]hydrazide (H_2L) and its dioxomolybdenum(VI) complex $[MoO_2L(OH_2)]$ was reported.



SCH. 1. H_2L.

EXPERIMENTAL

Salicylaldehyde and (4-nitrophenoxy)acetic acid hydrazide were obtained from Aldrich (Jingchu University of Technology, China). The remaining chemicals and solvents were of analytical reagent grade, and were purchased from Beijing Chemical Reagent Company (China). Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer (Jingchu University of Technology, China). X-ray measurement was performed using a Bruker Smart 1000 CCD diffractometer (Wuhan University, China) with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

Syntheses of the Compound $[MoO_2L(OH_2)]\cdot H_2L$

Salicylaldehyde (0.25 g, 2 mmol) and (4-nitrophenoxy)acetic acid hydrazide (0.43 g, 2 mmol) were mixed in methanol (30 mL). The mixture was stirred for 30 min at room temperature. To the above solution, a methanolic solution (20 mL) of $MoO_2(acac)_2$ (0.33 g, 1 mmol) was added. The final mixture was further stirred for 30 min to give a brown solution. Single crystals suitable for X-ray diffraction were formed by slow evaporation of the solution of the compound in air for a few days. Yield: 53%. Anal. Calcd. for $C_{30}H_{26}MoN_6O_{13}$: C, 46.5; H, 3.4; N, 10.9. Found: C, 46.7; H, 3.5; N, 10.8%.

Received 9 January 2012; accepted 23 December 2012.

The author acknowledges the Jingchu University of Technology for financial support.

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X-Ray Structure Determination

X-ray measurement was performed by using the ω-scan technique. Determination of the Laue class, orientation matrix, and cell dimensions were performed according to the established procedures where Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a wide range of 2 θ angles. The positions of non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The water H atoms in [$MoO_2L(OH_2)$] and the amino and hydroxyl H atoms in H_2L were located from a difference Fourier map and refined isotropically, with O—H, N—H, and H···H distances restrained to 0.85(1), 0.90(1), and 1.37(2) Å, respectively. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with the aid of the SHELXS-97 and SHELXL-97 suite of codes.[20, 21] The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonding information is given in Table 3.

RESULTS AND DISCUSSION

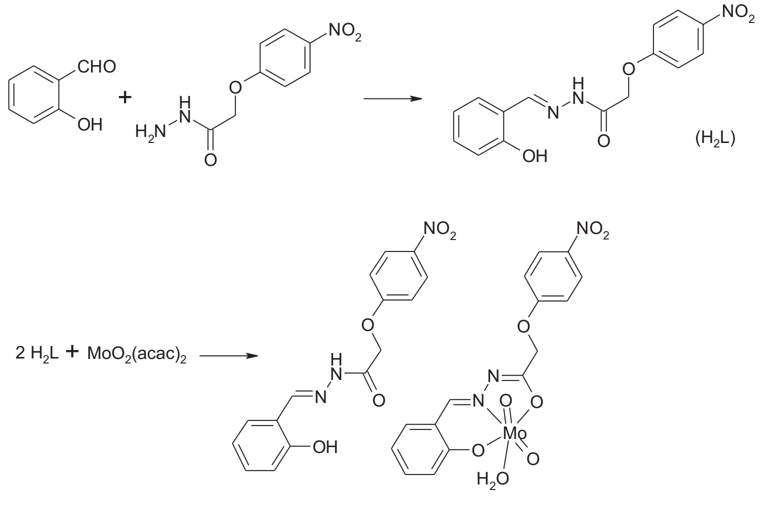
The compound was prepared by the reaction of $MoO_2(acac)_2$ with H_2L in methanol in a 1:2 mole proportion at room temperature (Scheme 2). The excess of the ligand was aggregate to the dioxomolybdenum(VI) complex molecule during the crystallization. The chemical formula of the compound was confirmed by elemental analyses and single-crystal X-ray diffraction.

Structure Description of the Compound

The molecular structure of the compound is shown in Figure 1. The asymmetric unit of the compound contains a

TABLE 1
Crystal data for the compound

Chemical formula	$C_{30}H_{26}MoN_6O_{13}$
Moiety formula	$C_{15}H_{13}MoN_3O_8 \cdot C_{15}H_{13}N_3O_5$
Fw	774.5
Crystal shape/color	Block/yellow
Crystal size (mm)	0.27 × 0.23 × 0.23
T (K)	298(2)
λ (MoKα) (Å)	0.71073
Crystal system	Triclinic
Space group	*P*–1
a (Å)	8.087(1)
b (Å)	13.681(2)
c (Å)	16.035(2)
α (°)	113.362(2)
β (°)	91.857(2)
γ (°)	100.691(2)
V (Å^3)	1589.2(4)
Z	2
μ (MoKα) (mm^{-1})	0.491
T_{min}	0.879
T_{max}	0.895
D_c (g cm^{-3})	1.619
Measured reflections	9068
Reflections/parameters	6491/463
Unique reflections	4881
Restraints	5
Goodness of fit on F^2	1.064
R_{int}	0.0292
R_1 [$I \geq 2\sigma(I)$]	0.0468
wR_2 [$I \geq 2\sigma(I)$]	0.0975
R_1 (all data)	0.0688
wR_2 (all data)	0.1084



SCH. 2. The preparation of the compound.

TABLE 2
Selected bond lengths (Å) and angles (°) for the compound

$[MoO_2L(OH_2)]$			
Bond lengths			
Mo1-O1	1.916(2)	C7-N1	1.290(4)
Mo1-O2	2.002(2)	N1-N2	1.403(4)
Mo1-N1	2.244(3)	N2-C8	1.283(4)
Mo1-O11	1.680(2)	O2-C8	1.320(4)
Mo1-O12	1.702(2)	C2-O1	1.359(4)
Mo1-O13	2.331(2)		
Bond angles			
O11-Mo1-O12	104.6(1)	O11-Mo1-O1	98.1(1)
O12-Mo1-O1	103.1(1)	O11-Mo1-O2	96.6(1)
O12-Mo1-O2	98.4(1)	O1-Mo1-O2	149.8(1)
O11-Mo1-N1	94.4(1)	O12-Mo1-N1	159.5(1)
O1-Mo1-N1	81.3(1)	O2-Mo1-N1	71.4(1)
O11-Mo1-O13	172.6(1)	O12-Mo1-O13	82.4(1)
O1-Mo1-O13	82.5(1)	O2-Mo1-O13	79.7(1)
N1-Mo1-O13	78.3(1)		
H_2L			
Bond lengths			
C22-N4	1.276(4)	O7-C23	1.222(4)
N4-N5	1.384(4)	C17-O6	1.351(5)
N5-C23	1.339(4)		

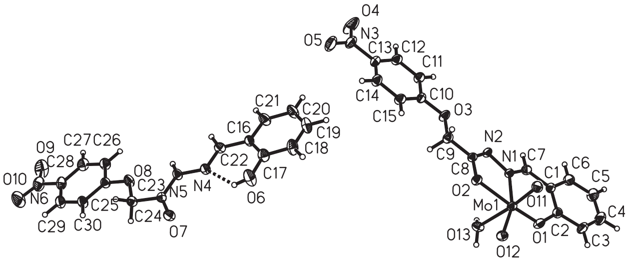


FIG. 1. Molecular structure of the compound with 30% probability thermal ellipsoids. Left: H_2L; Right: $[MoO_2L(OH_2)]$. Intramolecular O–H···N hydrogen bond is drawn as a dashed line.

free hydrazone molecule and a dioxomolybdenum(VI) complex molecule. In the hydrazone molecule, there forms an intramolecular O6–H6A···N4 hydrogen bond. The dihedral angle between the C16-C21 and C25-C30 benzene rings is 3.4(3)°. The plane defined by O9, N6, and O10 atoms forms a dihedral angle of 4.8(3)° with the C25-C30 benzene ring. The torsion angle of C22-N4-N5-C23, N4-N5-C23-C24, and N5-C23-C24-O8 are 2.3(3)°, 0.8(3)°, and 4.8(3)°, respectively. In the dioxomolybdenum(VI) complex molecule, the Mo atom is coordinated by one phenolate O, one imino N, and one enolic O atoms of the hydrazone ligand, two oxo O atoms, and one water O atom, forming an octahedral coordination. The displacement of the Mo atom from the equatorial mean plane defined by the O1, O2, O12, and N1 atoms toward the apical oxo atom O11 is 0.301(1) Å. The hydrazone ligand is coordinated to the Mo atom in its dianionic form, generating five- and six-membered chelate rings with angles of 71.4(1) and 81.3(1)°, respectively. The dihedral angle between the C1-C6 and C10-C15 benzene rings in the hydrazone ligand of the complex molecule is 7.6(3)°. The plane defined by O4, N3, and O5 atoms forms a dihedral angle of 2.4(3)° with the C10-C15 benzene ring. The enolate form of the ligand is evident from the N2–C8 and O2–C8 bond lengths with values of 1.283(4) and 1.320(4) Å, respectively, which are much different from the corresponding bonds of the free hydrazone molecule [N5–C23 = 1.339(4) Å, O7–C23 = 1.222(4) Å]. The coordinate bond lengths around the Mo atom are comparable to the values observed in similar dioxomolybdenum(VI) complexes.[22–24]

In the crystal structure of the compound, the free hydrazone molecules and the dioxomolybdenum(VI) complex molecules are linked through intermolecular O–H···O, O–H···N, and N–H···O hydrogen bonds, to form 2D layers parallel to the *ab* plane (Figure 2).

TABLE 3
Distances (Å) and angles (°) involving hydrogen bonding of the compound

D–H···*A*	*d* (*D*–H)	*d* (H··*A*)	*d* (*D*···*A*)	Angle (*D*–H···*A*)
O6–H6A···N4	0.84(1)	1.96(3)	2.619(4)	134(4)
O13–H13A)···O7$^{\#1}$	0.84(1)	1.93(2)	2.768(3)	173(4)
O13–H13B···O3$^{\#2}$	0.84(1)	2.64(3)	3.264(3)	132(4)
O13–H13B···N2$^{\#2}$	0.84(1)	2.05(2)	2.855(4)	160(4)
N5–H5···O12$^{\#3}$	0.90(1)	2.22(2)	3.082(4)	161(4)

Symmetry codes: #1: 2 – *x*, 1 – *y*, 1 – *z*; #2: 1 – *x*, – *y*, – *z*; #3: *x*, *y*, 1 + *z*.

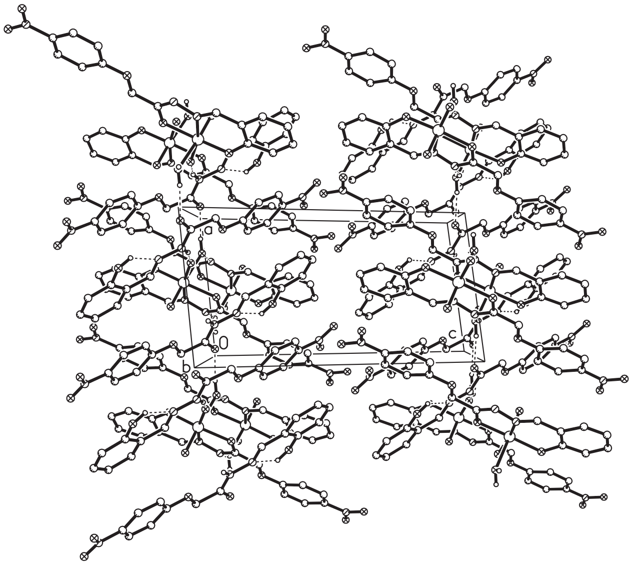


FIG. 2. Molecular packing of the compound, viewed along the *b*-axis. Hydrogen bonds are drawn as dashed lines.

CONCLUSION

In summary, a novel aggregation of (4-nitrophenoxy)acetic acid [1-(2-hydroxyphenyl)methylidene]hydrazide and its dioxomolybdenum(VI) complex has been obtained. The structure of the compound was characterized by elemental analysis and single-crystal X-ray diffraction method. The hydrazone ligand coordinates to the Mo atoms through the phenolic O, imino N, and enolic O atoms.

SUPPLEMENTARY MATERIALS

CCDC 861282 contains the supplementary crystallographic data for the complex. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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