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Synthesis and Crystal Structures of N'-(3,5-Dichlorosalicylidene)-4-nitrobenzohydrazide and Its Dioxomolybdenum(VI) Complex

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hydrazone compound N'-(3,5-dichlorosalicylidene)-4-Α nitrobenzohydrazide and its dioxomolybdenum(VI) complex have been synthesized and characterized by elemental analyses, infrared spectroscopy, and single-crystal X-ray determinations. The ligand crystallized in the monoclinic space group $P2_1/n$, with $a = 7.402(1), b = 13.429(2), c = 16.668(2) \text{ Å}, \beta = 99.718(2)^{\circ},$ V = 1633.0(4) Å³, Z = 4, R_1 = 0.0359, and wR_2 = 0.0811. The complex crystallized in the monoclinic space group $P2_1/c$, with $a = 13.443(1), b = 7.222(1), c = 18.997(2) \text{ Å}, \beta = 91.889(2)^\circ$ V = 1843.2(3) Å³, Z = 4, R_1 = 0.0289, and wR_2 = 0.0652. The asymmetric unit of the ligand contains a hydrazone molecule and a methanol molecule. In the complex, the Mo atom is coordinated by one hydrazone ligand, one methanol molecule, and two oxo O atoms, forming an octahedral coordination. The ligand coordinates to the Mo atom through the phenolate O, imine N, and enolic O atoms.

Supplemental materials are available for this article. Go to the publisher's online edition of Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry to view the supplemental file.

Keywords coordination compound, crystal structure, hydrazone, hydrogen bonding, molybdenum complex

INTRODUCTION

Hydrazones are a kind of special Schiff bases, which have been received considerable attention in biological and medicinal chemistry. The compounds show effective antibacterial, antifungi, and antitumor activities.^[1–5] In recent years, a large number of complexes derived from Schiff bases have been reported. The complexes show interesting biological, catalytic, magnetic, and many other properties.^[6–10] However, the number of complexes derived from hydrazones is rare. Most of the molybdenum complexes derived from hydrazone ligands have been proved to have catalytic properties.^[11–13] In this study, a hydrazone ligand N'-(3,5-dichlorosalicylidene)-4-nitrobenzohydrazide (1) and its dioxomolybdenum(VI) complex have (2), have been synthesized and characterized. The particular interest is to investigate the coordination of the hydrazone ligand to the Mo atom.

EXPERIMENTAL

Materials and Methods

3,5-Dichlorosalicylaldehyde and 4-nitrobenzohydrazide were obtained from Fluka (Jiaxing University, P. R. China). Other solvents and reagents were obtained commercial and were used without further purification. IR spectra of KBr discs were recorded with a Perkin-Elmer 783 spectrometer (Jiaxing University, P. R. China). Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer (Jiaxing University, P. R. China).

Synthesis of N'-(3,5-Dichlorosalicylidene)-4-nitrobenzohydrazide (1)

3,5-Dichlorosalicylaldehyde (1.0 mmol, 0.19 g) and 4nitrobenzohydrazide (1.0 mmol, 0.18 g) were mixed and stirred in absolute methanol (30 mL). The reaction mixture was refluxed for 1 h on a water bath, then cooled to room temperature. Colorless block-like single crystals of the compound were obtained by slow evaporation of the solution in air. Yield, 72%. Anal. Calcd. (%) for $C_{14}H_9Cl_2N_3O_4$: C, 47.5; H, 2.6; N, 11.9. Found (%): C, 47.3; H, 2.5; N, 11.8.

Synthesis of the Complex (2)

To a methanolic solution (20 mL) of the ligand (0.5 mmol, 0.18 g) was added a methanolic solution (20 mL) of $MoO_2(acac)_2$ (0.5 mmol, 0.13 g) with stirring. The mixture was stirred for 30 min at room temperature to give a yellow solution. After keeping the solution in air for five days, yellow block-shaped crystals of (2), suitable for X-ray crystal structural

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 TABLE 1

 Crystallographical and experimental data for (1) and (2)

Compound	(1)	(2)
Formula	C ₁₅ H ₁₃ Cl ₂ N ₃ O ₅	C ₁₅ H ₁₁ Cl ₂ MoN ₃ O ₇
Mr	386.2	512.1
<i>T</i> (K)	298(2)	298(2)
Crystal shape/color	block/colorless	block/yellow
Crystal size/mm ³	$0.15 \times 0.13 \times 0.13$	$0.17 \times 0.15 \times 0.15$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a /Å	7.402(1)	13.443(1)
b /Å	13.429(2)	7.222(1)
c /Å	16.668(2)	18.997(2)
β /°	99.718(2)	91.889(2)
$V/Å^3$	1633.0(4)	1843.2(3)
Ζ	4	4
$Dc /(g/cm^{-3})$	1.571	1.845
μ (MoK α) (cm ⁻¹)	0.431	1.046
<i>F</i> (000)	792	1016
R _{int}	0.0457	0.0306
Measured reflections	16738	19209
Unique reflections	3041	3424
Observed reflections $I \ge 2\sigma(I)$	2242	2814
Min. and max. transmission	0.9382/0.9461	0.8422/0.8588
Parameters	232	256
Goodness-of-fit on F^2	1.019	1.055
$R_1, wR_2 \ [I \ge 2\sigma(I)]^a$	0.0359, 0.0811	0.0289, 0.0652
R_1 , wR_2 (all data) ^a	0.0606, 0.0915	0.0423, 0.0733
Large diff. peak and hole $/(e.Å^{-3})$	0.191/-0.237	0.756/-0.452

 ${}^{a}R_{1} = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|, wR_{2} = [\Sigma w (Fo^{2} - Fc^{2})^{2} / \Sigma w (Fo^{2})^{2}]^{1/2}, w_{(1)} = [\sigma^{2} (Fo)^{2} + (0.0408 (Fo^{2} + 2Fc^{2})/3)^{2} + 0.5378 (Fo^{2} + 2Fc^{2})/3)]^{-1}, w_{(2)} = [\sigma^{2} (Fo)^{2} + (0.028 (Fo^{2} + 2Fc^{2})/3)^{2} + 2.4883 (Fo^{2} + 2Fc^{2})/3)]^{-1}.$

determination, were formed at the bottom of the vessel on slow evaporation of the solution in air. Yield, 51%. Anal. Calcd. (%) for $C_{15}H_{11}Cl_2MoN_3O_7$: C, 35.2; H, 2.2; N, 8.2. Found (%): C, 35.0; H, 2.2; N, 8.3.

X-Ray Structural Determination

Diffraction intensities for the ligand and the complex were collected at 298(2) K using a Bruker Apex II CCD area detector (Zhejiang University, P. R. China) with Mo-K α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,^[14] and empirical absorption corrections were performed using the SADABS program.^[15] The structures were solved by direct methods and refined against F^2 by fullmatrix least-squares methods using SHELXTL.^[16] All of the non-hydrogen atoms were refined anisotropically. The amino H atom in (1) and the methanol H atom in (2) were located in difference Fourier maps and refined isotropically, with N–H and O–H distances restrained to 0.90(1) and 0.85(1) Å, respec-

tively. The remaining H atoms were placed in geometrically ideal positions and constrained to ride on their parent atoms. The crystallographic data for the compounds are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3.

RESULTS AND DISCUSSION

The hydrazone ligand was prepared by the condensation reaction of 3,5-dichlorosalicylaldehyde with 4-nitrobenzohydrazide in methanol (Scheme 1). The ligand crystallized as colorless single crystals, which are stable in air at room temperature, and soluble in DMSO, DMF, MeOH, EtOH, and MeCN. The complex was prepared by the reaction of the hydrazone ligand with $MoO_2(acac)_2$ in methanol (Scheme 2), with color change from colorless to yellow. Single crystals of the complex are also stable in air at room temperature, soluble in DMF, DMSO, MeOH, EtOH, and MeCN.



SCH. 1. The synthesis of the ligand.



SCH. 2. The synthesis of the complex.

TABLE 2 Selected bond lengths (Å) and angles (°) for (1) and (2)

	(1)		
C7-N1	1.278(2)	N1-N2	1.378(2)
N2-C8	1.356(3)	C8-O2	1.223(2)
	(2)		
C7-N1	1.282(4)	N1-N2	1.395(3)
N2-C8	1.296(4)	C8-O2	1.320(3)
Mo1-O1	1.925(2)	Mo1-O2	1.996(2)
Mo1-O5	1.677(2)	Mo1-O6	1.701(2)
Mo1-O7	2.358(2)	Mo1-N1	2.240(2)
O5-Mo1-O6	105.30(12)	O5-Mo1-O1	99.44(11)
O6-Mo1-O1	105.08(10)	O5-Mo1-O2	99.31(10)
O6-Mo1-O2	95.87(9)	O1-Mo1-O2	146.94(9)
O5-Mo1-N1	91.17(11)	O6-Mo1-N1	161.05(11)
O1-Mo1-N1	80.83(8)	O2-Mo1-N1	71.81(8)
O5-Mo1-O7	167.80(10)	O6-Mo1-O7	86.52(10)
O1-Mo1-O7	79.95(8)	O2-Mo1-O7	76.05(8)
N1-Mo1-O7	76.68(9)		

TABLE 3Hydrogen bonding information

		-		
D−H···A	<i>D</i> —Н (Å)	H···A (Å)	$D \cdots A$ (Å)	$D-\mathrm{H}\cdots A$ (°)
		(1)		
N2−H2···O5	0.90(1)	1.93(1)	2.799(2)	163(3)
$O5-H5\cdots O2^i$	0.82	2.15	2.902(2)	153
O1−H1···N1	0.82	1.92	2.636(2)	145
		(2)		
$O7-H7\cdots O6^{ii}$	0.84(1)	2.10(1)	2.937(3)	176(4)

Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) 1 - x, -1/2 + y, 1/2 - z.

IR Spectra of (1) and (2)

The IR spectra of the hydrazone ligand and its dioxomolybdenum complex provide information about the metal-ligand bonding. The weak and broad absorptions centered at 3453 and 3421 cm⁻¹, respectively, for the ligand and the complex are assigned to the O–H vibrations of the hydroxyl group or methanol molecules. The sharp band at 3127 cm⁻¹ indicative of the N–H bond in the spectrum of the ligand is absent in the complex, indicating the coordination of the ligand to the Mo atom through enolic form. The hydrazone ligand shows stretching bands attributed to C=O, C=N, and C–OH at 1653, 1645, and 1180 cm⁻¹, respectively. The Mo=O stretching modes occur as a pair of sharp strong bands at 932 and 869 cm⁻¹, assigned to the antisymmetric and symmetric stretching mode of the MoO₂ moiety. The strong band indicative of the –C=N–N=C– group in the complex is observed at 1603 cm⁻¹.

Structure Description of (1) and (2)

Figures 1 and 2 give perspective views of the ligand and the complex together with the atomic labeling systems. The asymmetric unit of (1) contains a hydrazone molecule and a methanol molecule. There is an intramolecular O-H···N hydrogen bond in the hydrazone molecule, which contribute to the planarity of the molecule. The dihedral angle between the two benzene rings C1-C6 and C9-C14 in (1) is $6.0(2)^{\circ}$. The dihedral angle between the C9-C14 benzene ring and the plane defined by the nitro group is $2.0(2)^{\circ}$. In the crystal of (1), adjacent two hydrazone molecules are linked by two methanol molecules through $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds, to form dimers (Figure 3). The complex (2) is a mononuclear dioxomolybdenum(VI) complex derived from the ligand. The Mo atom is coordinated by one hydrazone ligand, one methanol molecule, and two oxo O atoms, forming an octahedral coordination. The Mo1 atom deviates from the plane defined by the



FIG. 1. The structure of (1), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.



FIG. 2. The structure of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



FIG. 3. The crystal packing of (1), viewed along the b axis. Hydrogen bonds are shown as dashed lines.



FIG. 4. The crystal packing of (2), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

equatorial donor atoms O1, O2, N1, and O6 by 0.320(1) Å toward the O5 atom. The hydrazone ligand coordinates to the Mo atom through the phenolate O1, imine N1, and enolic O2 atoms, generating a five- and a six-membered chelate rings. The dihedral angle between the C1-C6 and C9-C14 benzene rings in the complex is $3.6(2)^{\circ}$, and the dihedral angle between the C9-C14 benzene ring and the plane defined by the nitro group is $4.4(2)^{\circ}$, indicating the planarity of the ligand. The Mo1-O7 bond is much longer than the other bonds, which is common for similar dioxomolybdenum(VI) complexes with methanol ligands.^[11,17,18] In the crystals of (**2**), molecules are linked through intermolecular O–H···O hydrogen bonds, to form zigzag chains running along the *b* axis (Figure 4).

The hydrazone ligand coordinates to the Mo atom through the deprotonated and enolate form. The bond lengths of C7–N1, N1–N2, and C8–O2 in the complex are longer than those in the free ligand, together with the bond length of C8–N2 in the complex shorter than that in the free ligand, proving the coordination of the phenolate O, imine N, and enolate O atoms of the ligand.

CONCLUSION

A hydrazone compound N'-(3,5-dichlorosalicylidene)-4nitrobenzohydrazide and its dioxomolybdenum(VI) complex have been synthesized and structurally characterized. The hydrazone compound coordinates to the Mo atom through the phenolate O, imine N, and enolic O atoms. The complex may be used as interesting catalytic material, which deserves further study.

SUPPLEMENTARY MATERIALS

Crystallographic data for (1) and (2) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 895035 (1) and 895036 (2). Copies of these data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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