

Short communication

# Synthesis, Crystal Structure and Catalytic Property of a Cobalt(II) Compound Derived From 2-Bromo-*N'*-(2-Hydroxy-5-Methylbenzylidene)Benzohydrazide

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## Abstract

With a tridentate Schiff base ligand 2-bromo-*N'*-(2-hydroxy-5-methylbenzylidene)benzohydrazide (HL) and cobalt nitrate, a cobalt(II) compound  $[\text{Co}(\text{L})_2]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  (**1**) was prepared and characterized by elemental analysis, IR spectroscopy and X-ray structure determination. The compound crystallizes in the monoclinic space group  $P2_1/c$ . Single crystal X-ray diffraction analysis reveals that the Co atom is coordinated by the NOO donor atoms of the Schiff base ligands, in an octahedral coordination. The compound show effective catalytic oxidation property on some olefins. In general, oxidation of the substrates gave the corresponding epoxides in over 80% yields for various styrene and 71% for cyclohexene.

**Keywords:** Schiff base; Cobalt complex; Crystal structure; Catalytic property.

## 1. Introduction

In recent years, the catalytic oxidation of olefins has aroused much attention in the production of chemicals and fine chemicals since epoxides are key starting materials for a wide variety of oily products.<sup>1</sup> Because of the environment friendly nature  $\text{H}_2\text{O}_2$  has been regarded as the first selected oxidant in the oxidation of olefins. Transition metal complexes with various ligands have presented interesting catalytic properties.<sup>2</sup> Among the complexes, cobalt species show efficient catalytic oxidation properties.<sup>3</sup> Hydrazones are versatile ligands in coordination chemistry.<sup>4</sup> Recently, we have reported the catalytic property of a molybdenum complex with hydrazone ligand.<sup>5</sup> As an extension of the work on the exploration of new catalytic material, in this paper, a new cobalt(II) compound

derived from the Schiff base ligand 2-bromo-*N'*-(2-hydroxy-5-methylbenzylidene)benzohydrazide (HL) was prepared and its catalytic oxidation property was performed.

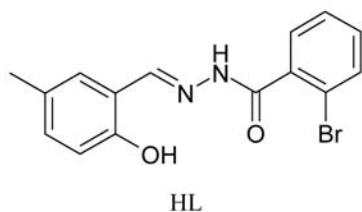
## 2. Experimental

### 2.1. Materials and Methods

5-Methylsalicylaldehyde and 2-bromobenzohydrazide were purchased from Alfa Aesar. Cobalt nitrate hexahydrate and solvents are commercially available and were used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. Infrared spectra were measured on KBr disks with a Hitachi I-5040 FT-IR spectrophotometer. Molar conductivity was determined in methanol with a concentration of  $10^{-3}$  M at room temperature on a DDS-11A conductometer.

### 2.2. Synthesis of the Compound

5-Methylsalicylaldehyde (0.136 g, 1.00 mmol) and 2-bromobenzohydrazide (0.215 g, 1.00 mmol) were mixed and stirred in methanol (20 mL) for 30 min. Then,



cobalt nitrate hexahydrate (0.291 g, 1.00 mmol) dissolved in methanol (20 mL) was added, and stirred for another 30 min. The solution was kept still in air for a few days to slowly evaporate in order to give brown block-shaped single crystals of **1**. Yield: 32%. Analysis: Found: C 45.27, H 3.13, N 8.97%. Calculated for  $C_{60}H_{50}Br_4Co_2N_{10}O_{15}$ : C 45.36, H 3.17, N 8.82%. IR (KBr,  $cm^{-1}$ ):  $\nu(O-H)$ , 3451;  $\nu(N-H)$ , 3217;  $\nu(C=N)$ , 1605;  $\nu(NO_3)$ , 1377 and 835.

### 2. 3. Catalytic Oxidation Experiment

Catalytic experiment was carried out in a 50 mL glass round-bottom flask fitted with a reflux condenser and placed in an oil bath at prearranged temperature under continuous stirring. The oxidation was carried out as follows: the compound **1** (0.032 mmol) was dissolved in 10 mL 1,2-dichloroethane. Then 10 mmol alkene was added to the reaction mixture and 30 mmol TBHP was added. The reaction mixture was refluxed for 1 h. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

### 2. 4. X-Ray Structure Determination

Data collection was performed with a Bruker Apex II CCD diffractometer at 298 K. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least squares (SHELXL-97) on  $F^2$ .<sup>6</sup> All non-hydrogens were refined anisotropically. Hydrogens were placed

geometrically and refined with a riding model, with isotropic displacement coefficients  $U(H) = 1.2 U(C)$  or  $1.5 U(C_{methyl})$ . Br1 atom is disordered over two sites, with occupancies of 0.727 and 0.273 and Br2 atom is disordered over two sites, with occupancies of 0.534 and 0.466. Atoms C12, C13, C14, C15, Br4, N9, O9, O10 and O11 were restrained using ISOR instruction. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1**

Co(1)–N(3)	1.994(7)	Co(1)–N(1)	2.002(7)
Co(1)–O(3)	2.034(6)	Co(1)–O(1)	2.036(6)
Co(1)–O(4)	2.042(6)	Co(1)–O(2)	2.083(6)
Co(2)–N(7)	1.987(7)	Co(2)–N(5)	2.011(7)
Co(2)–O(5)	2.029(6)	Co(2)–O(7)	2.049(5)
Co(2)–O(6)	2.068(6)	Co(2)–O(8)	2.120(6)
N(3)–Co(1)–N(1)	166.0(3)	N(3)–Co(1)–O(3)	88.0(3)
N(1)–Co(1)–O(3)	101.8(3)	N(3)–Co(1)–O(1)	102.9(3)
N(1)–Co(1)–O(1)	87.2(3)	O(3)–Co(1)–O(1)	89.2(2)
N(3)–Co(1)–O(4)	80.1(3)	N(1)–Co(1)–O(4)	90.3(3)
O(3)–Co(1)–O(4)	167.9(2)	O(1)–Co(1)–O(4)	90.9(2)
N(3)–Co(1)–O(2)	90.7(3)	N(1)–Co(1)–O(2)	79.4(3)
O(3)–Co(1)–O(2)	91.3(2)	O(1)–Co(1)–O(2)	166.4(2)
O(4)–Co(1)–O(2)	91.5(3)	N(7)–Co(2)–N(5)	166.7(3)
N(7)–Co(2)–O(5)	98.4(2)	N(5)–Co(2)–O(5)	88.7(3)
N(7)–Co(2)–O(7)	87.0(2)	N(5)–Co(2)–O(7)	104.3(2)
O(5)–Co(2)–O(7)	89.2(2)	N(7)–Co(2)–O(6)	94.8(3)
N(5)–Co(2)–O(6)	78.7(3)	O(5)–Co(2)–O(6)	166.7(2)
O(7)–Co(2)–O(6)	90.2(2)	N(7)–Co(2)–O(8)	78.8(3)
N(5)–Co(2)–O(8)	89.8(2)	O(5)–Co(2)–O(8)	91.9(2)
O(7)–Co(2)–O(8)	165.8(2)	O(6)–Co(2)–O(8)	92.0(2)

Table 1. Crystal data, data collection and structure refinement for **1**

Molecular Formula	$C_{60}H_{50}Br_4Co_2N_{10}O_{15}$
Formula weight	1588.6
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ (Å)	13.406(1)
$b$ (Å)	27.443(2)
$c$ (Å)	18.142(2)
$\beta$ (deg)	101.147(8)
$V$ (Å <sup>3</sup> )	6548.5(10)
$Z$	4
$D_c$ (g cm <sup>-3</sup> )	1.611
$F(000)$	3176
$\mu$ (mm <sup>-1</sup> )	3.019
Measured reflections	40016
Unique reflection	11962
Observed reflections [ $I > 2\sigma(I)$ ]	4969
$R_{int}$	0.1238
Parameters	831
Restraints	59
Final $R$ index [ $I > 2\sigma(I)$ ]	0.0793, 0.1678
$R$ index (all data)	0.2081, 0.2315
Goodness-of-fit on $F^2$	0.978

## 3. Results and Discussion

### 3. 1. Chemistry

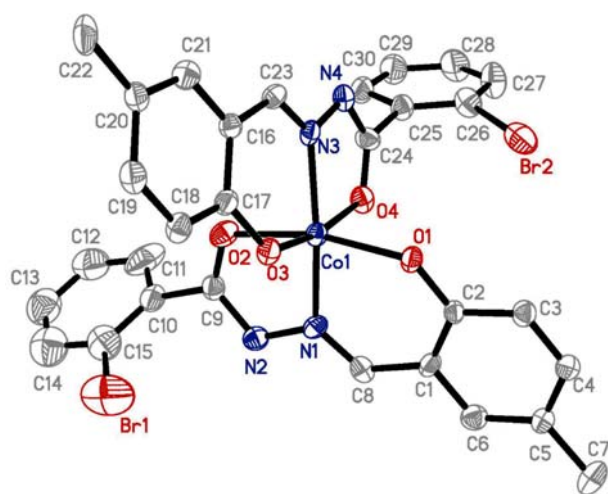
The compound **1** was prepared by the reaction of equimolar quantities of the Schiff base ligand with cobalt nitrate hexahydrate in methanol. Crystals of **1** are stable in air and soluble in methanol, ethanol, DMF and DMSO, but are insoluble in water. The molar conductance measured in methanol with a concentration of  $10^{-3}$  M is  $115 \Omega^{-1} cm^2 mol^{-1}$ , indicating the compound is a 1:1 electrolyte.<sup>7</sup>

### 3. 2. Infrared Spectra

The compound has been characterized by infrared spectroscopy. The broad band centered at  $3451 cm^{-1}$  is assigned to the O–H vibrations. The sharp band at  $3217 cm^{-1}$  is assigned to the N–H vibration of the amino groups. The strong band indicative of the C=N group is observed at  $1605 cm^{-1}$ .<sup>8</sup> The bands indicative of the nitrate anions are located at  $1377$  and  $835 cm^{-1}$ .

### 3. 3. Crystal Structure Description of 1

The asymmetric unit of **1** contains two mononuclear cobalt(II) complex cations, two nitrate anions and one water molecule of crystallization. The Co(1) complex cation of the compound is shown in Figure 1. Since the geometries of both complex cations are very similar, the Co(2) complex cation of the compound is shown in Figure S1 as a supplementary material. The Co atoms are coordinated by two phenolate O, two imine N and two carbonyl O atoms from two Schiff base ligands, forming octahedral coordination. The distortion of the octahedral coordination can be observed from the *cis* and *trans* coordinate bond angles, *viz.* 79.4(3)–102.9(3)° and 166.0(3)–167.9(2)° for Co(1), 78.8(3)–104.3(2)° and 165.8(2)–166.7(3)° for Co(2). The bond lengths related to the Co atoms are similar to each other, and also comparable to those observed in cobalt complexes with Schiff base ligands.<sup>9</sup> The dihedral angles between the two benzene rings of the Schiff base ligands C(1)–C(6) and C(10)–C(15), C(16)–C(21) and C(25)–C(30), C(31)–C(36) and C(40)–C(45), C(46)–C(51) and C(55)–C(60) are 105.4(5), 74.8(5), 35.9(5), and 62.4(5)°, respectively.

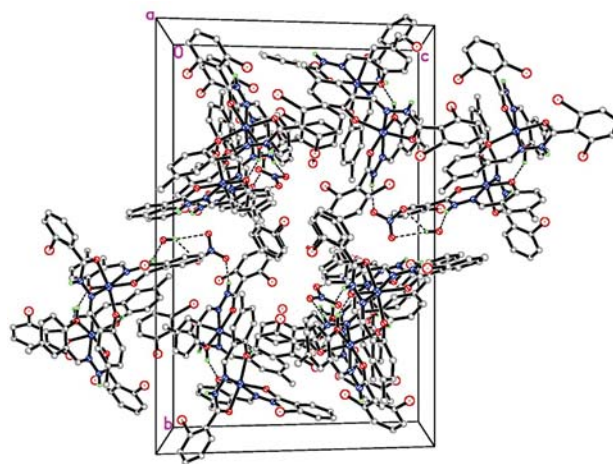


**Figure 1.** The molecular structure of the Co1 complex cation with 30% probability thermal ellipsoids.

In the crystal structure of **1**, two adjacent complex cations are linked by O(7)–H(7D)···O(3) and O(1)–H(1A)···O(5) hydrogen bonds (Table 3), to form a dimer. The dimers are further linked by nitrate anions through N(4)–H(4A)···O(13), O(15)–H(15B)···O(9), O(15)–H(15B)···O(11), N(8)–H(8A)···O(12), N(6)–H(6A)···O(15) and N(2)–H(2A)···O(10) hydrogen bonds (Table 3), to form chains, as shown in Figure 2.

### 3. 4. Catalytic Property

The catalytic results are given in Table 3. As seen from the results, the products of the reactions are epoxides and the selectivities for these products are 100%. High TONs (turn over numbers = moles of substrate converted per mole of **1**) obtained for the substrates suggest a very high catalytic efficiency for **1**. In general, oxidation of the substrates gave the corresponding epoxides in over 80% yields for various styrene and 71% for cyclohexene. The catalytic property of the compound is comparable to the oxidovanadium(V) complex.<sup>10</sup>





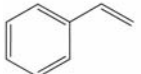
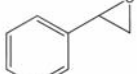
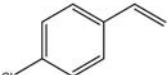
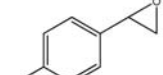
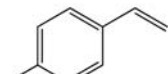
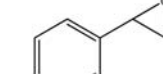
**Figure 2.** Molecular packing structure of **1**, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

**Table 3.** Distances (Å) and angles (°) involving hydrogen bonding in **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	Angle D–H···A
O(7)–H(7D)···O(3)	0.93	1.65	2.442(7)	141
O(1)–H(1A)···O(5)	0.93	1.63	2.463(7)	146
N(4)–H(4A)···O(13) <sup>i</sup>	0.86	2.00	2.85(1)	170
O(15)–H(15B)···O(9) <sup>ii</sup>	0.85	2.38	3.20(2)	163
O(15)–H(15B)···O(11) <sup>ii</sup>	0.85	2.23	2.88(1)	133
N(8)–H(8A)···O(12) <sup>ii</sup>	0.86	1.96	2.79(1)	163
N(6)–H(6A)···O(15)	0.86	1.98	2.80(1)	159
N(2)–H(2A)···O(10)	0.86	1.94	2.78(1)	168

Symmetry codes: i: 1 + *x*, ½ – *y*, –½ + *z*; ii: *x*, ½ – *y*, –½ + *z*.

Table 3. Catalytic oxidation results<sup>a</sup>

Substrate	Product	Conversion (%) <sup>b</sup>	TON <sup>c</sup>
		71	287
		83	315
		88	353
		81	327

<sup>a</sup> The molar ratio of catalyst:substrate:TBHP is 1:300:1000. The reactions were performed in mixture of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (V:V = 6:4; 1.5 mL).

<sup>b</sup> The GC conversion (%) was measured relative to the starting substrate after 1 h.

<sup>c</sup> TON: turn over number = moles of substrate converted per mole of **1**.

## 4. Conclusions

In summary, a new mononuclear cobalt(II) compound with a tridentate Schiff base ligand 2-bromo-*N*'-(2-hydroxy-5-methylbenzylidene)benzohydrazide has been prepared and characterized. Single crystal structure of the compound was determined. The Co atom in the complex cation is in an octahedral coordination. Single crystal of the compound is stabilized by hydrogen bonds. The compound show effective catalytic oxidation property on some olefins. In general, oxidation of the substrates gave the corresponding epoxides in over 80% yields for various styrene and 71% for cyclohexene.

## 5. Supplementary Material

CCDC-1448088 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 6. Acknowledgments

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## Povzetek

Kobaltovo(II) spojino  $[\text{Co}(\text{L})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$  (**1**) smo pripravili iz trovezne Schiffove baze 2-bromo-*N'*-(2-hidroksi-5-metilbenziliden)benzohidrazidom (HL) in kobaltnim nitratom ter jo okarakterizirali z elementno analizo, IR spektroskopijo in rentgensko strukturno analizo. Spojina kristalizira v monoklinski prostorski skupini  $P2_1/c$ . Monokristalna rentgenska difrakcija je razkrila, da je Co atom oktaedrično koordiniran z NOO donorskimi atomi Schiffove baze. Spojina ima učinkovite katalitične lastnosti za oksidacijo nekaterih olefinov. Na splošno, oksidacije substratov dajo ustrezne epoksidge z več kot 80% izkoristkom pri različnih stirenih in 71% pri cikloheksenu.