

## 钴的二苯甲酰甲烷配合物: 晶体结构及其轴向置换反应

卢会杰<sup>1</sup> 高洁<sup>1</sup> 杜晨霞<sup>1</sup> 樊耀亭<sup>\*1</sup> 侯红卫<sup>1</sup> 丁德刚<sup>1</sup> 翟俊玲<sup>2</sup>

(<sup>1</sup> 郑州大学化学系, 郑州 450052)

(<sup>2</sup> 三门峡职业技术学院, 三门峡 472000)

关键词: 二苯甲酰甲烷 钴配合物 晶体结构 轴向置换反应  
分类号: 0614.81

### Cobalt (II) Complexes of Dibenzoylmethane(Hdbm): Crystal Structures and Axial Metathetical Reaction of the Complexes with Pyridine or its Derivatives

LU Hui-Jie<sup>1</sup> GAO Jie<sup>1</sup> DU Chen-Xia<sup>1</sup> FAN Yao-Ting<sup>\*1</sup> HOU Hong-Wei<sup>1</sup> DING De-Gang<sup>1</sup> ZHAI Jun-Ling<sup>2</sup>

(<sup>1</sup> Department of Chemistry, Zhengzhou University, Zhengzhou 450052)

(<sup>2</sup> Sanmenxia College of Professional Technology, Sanmenxia 472000)

Cobalt (II) can form complexes with Hdbm in different environments. Hdbm reacted with cobalt nitrate to give complex **1** [Co(dbm)<sub>2</sub> · 2H<sub>2</sub>O]. When complex **1** reacted with pyridine,  $\alpha$ -stilbazole or 4, 4'-bipyridine respectively, complex **2** [Co(DBM)<sub>2</sub>Py<sub>2</sub>] (Py = pyridine), **3** [Co(DBM)<sub>2</sub>Sbz<sub>2</sub>] (Sbz =  $\alpha$ -stilbazole) or **4** [Co(DBM)<sub>2</sub>BPy]<sub>n</sub> was obtained in turn through metathetical reaction. The coordination modes are octahedral polyhedrons. In the crystal structures, the two dbms take the plane position and two other donor molecules take the axial position. CCDC: 196070 for complex **2**; 186859 for complex **3**.

Keywords: dibenzoylmethane cobalt complexes crystal structures axial metathetical reaction

## 0 Introduction

Dibenzoylmethane(Hdbm), as a kind of  $\beta$ -diketone, has been widely used in determination of metal ions<sup>[1-5]</sup>. By synergistic extraction under certain experimental conditions, cobalt<sup>[2]</sup> and other metal ions<sup>[1, 3-5]</sup> can be selectively determined with HDBM. The cobalt (II) complex of HDBM has also been reported of catalyzing the oxidation of olefins to ketones<sup>[6]</sup>. These characters are based on the formation of complexes of

metal ions with HDBM. To understand better the complexation behavior of HDBM with cobalt, some properties (magnetic susceptibility, mössbauer spectra) of the complexes have been reported<sup>[7, 8]</sup>, but little is known about the structures of the complexes. In this paper, we present the preparation of cobalt (II) complexes with mixed ligands of HDBM and pyridine derivatives (or H<sub>2</sub>O) and describe the crystal structures of two complexes, [Co(DBM)<sub>2</sub>Py<sub>2</sub>] (**2**, Py = pyridine) and [Co(DBM)<sub>2</sub>Sbz<sub>2</sub>] (**3**, Sbz =  $\alpha$ -stilbazole). In the

收稿日期: 2002-07-28。收修改稿日期: 2002-11-11。

国家自然科学基金资助项目(No. 29871025, 20171040)。

\* 通讯联系人。E-mail: yt.fan@371.net

第一作者: 卢会杰, 男, 40岁, 教授, 研究方向: 功能配合物和有机合成。

preparation of these complexes, metathetical reactions were observed of the ligands which occupied the axial positions, and the result is also discussed.

## 1 Experimental

Elemental analyses were performed on a Carlo-Erba 1106 analyzer. All chemicals were purchased as AR reagents and were used without further purification.  $\alpha$ -Stilbazole was prepared according to the literature method<sup>[9]</sup>.

### 1.1 Preparation of Dibenzoylmethane(HDBM)

To the suspension of sodium methoxide (5.4g, 0.1mol) in toluene (100mL) was added a mixture of acetophenone (12g, 0.1mol) and methyl benzoate (13.6g, 0.1mol) dropwise with stirring. After addition, the system was stirred and refluxed for 2h. Upon cooling and neutralization with dilute hydrochloric acid, the organic phase was separated, dried over sodium sulphate. After distillation of toluene, the residue was distilled at reduced pressure (218 ~ 220°C/18mm) to give HDBM (18g, 80%) as an oil. The oil solidified on standing. The product was recrystallized from methanol to give a light yellow needle, m. p. 77°C. Anal. Calcd. for  $C_{15}H_{12}O_2$  (%): C, 80.36; H, 5.36. Found: C, 80.47; H, 5.65. <sup>1</sup>H NMR( $CDCl_3$ ),  $\delta$  4.64(s,  $CH_2$ ); 6.87(s,  $C=CH$ ); 7.48 ~ 7.58(m, Ar-H); 7.98 ~ 8.00(m, Ar-H).

### 1.2 Preparation of Cobalt Complexes with HDBM

To a mixture of 1mmol  $Co(NO_3)_2 \cdot 6H_2O$  (291g) and 2mmol HDBM (448mg) in 30mL 95% ethanol was added 1.5mL 5% solution of sodium hydroxide with stirring. After addition, the system was allowed to stand overnight. A red solid  $Co(DBM)_2 \cdot 2H_2O$  (1) was obtained on filtration. Anal. Calcd. for  $[CoC_{30}H_{24}O_2]$  (%): C, 75.79; H, 5.05. Found: C, 75.55; H, 4.96.

To a solution of 0.2mmol (95mg)  $Co(DBM)_2 \cdot 2H_2O$  in 10mL ethanol was added a few drops of pyridine with stirring. The mixture was stirred for 10min and was filtered to remove any insoluble material. The filtrate was allowed to stand for slow evaporation to

provide red prism crystals  $[Co(DBM)_2Py_2]$  (2). Anal. Calcd. for  $CoC_{40}H_{32}N_2O_4$  (%): C, 72.40; H, 4.83; N, 4.22. Found: C, 72.55; H, 4.93; N, 4.42.

A solution of 0.4mmol (72.5mg) Sbz in 15mL ethanol was added to the solution of 0.2mmol (95mg)  $Co(DBM)_2 \cdot 2H_2O$  in 10mL ethanol. The mixture was stirred for about 10min and then filtered to remove any insoluble materials. The filtrate was allowed to stand for slow evaporation to provide red-brown crystals  $[Co(DBM)_2Sbz_2]$  (3). Anal. Calcd. for  $CoC_{56}H_{44}N_2O_4$  (%): C, 77.51; H, 5.07; N, 3.23. Found: C, 77.55; H, 4.99; N, 3.44.

A solution of 0.2mmol 4, 4'-bipyridine (BPy) in 15mL ethanol was added dropwise with stirring to the solution of 0.2mmol (95mg)  $Co(DBM)_2 \cdot 2H_2O$  in 10mL ethanol. A red brown solid was precipitated during the addition. The solid was dissolved in DMF. And by a slow diffusion of ether to the above solution, clusters of fine needles,  $[Co(DBM)_2BPy]_n$  (4), were obtained. Anal. Calcd. for  $CoC_{40}H_{30}N_2O_4$  (%): C, 72.62; H, 4.54; N, 4.24. Found: C, 72.57; H, 4.94; N, 4.44.

Complexes 2 and 3 could also be obtained by following method:

A solution of 2mmol pyridine (or 2mmol  $\alpha$ -Stilbazole) in 20mL ethanol was added with stirring to the solution of 1mmol  $Co(NO_3)_2$  and 2mmol HDBM in 20mL ethanol. After stirring for 10min, the mixture was filtered to remove any insoluble material. The filtrate was allowed to stand for slow evaporation to provide the corresponding complexes. Results of elemental analyses showed that the composition of the products were the same as complexes 2, 3 and 4, respectively.

### 1.3 X-Ray Crystal Structure Determination

A suitable crystal of complex 2 (dimensions 0.40 × 0.40 × 0.30mm) or 3 (dimensions 0.30 × 0.20 × 0.20mm) was mounted on a glass fibre. All measurements were made on Rigaku-Raxis-IV imaging plate with graphite monochromated  $MoK\alpha$  radiation ( $\lambda = 0.71073\text{Å}$ ). Data were collected at room temperature to a maximum  $2\theta$  value of 55°. A total of 30 oscillation images with 5.00° oscillation were collected, each

being exposed for 15.0min. The crystal to detector distance was 110mm with the detector at the zero swing position. Readout was performed in the 0.100mm pixel mode. A total of 4795 reflections for complex **2** [or 3529 reflections for complex **3**] were collected, the intensity data were corrected for Lorentz-polarization factors as well as for absorption. Structures were solved by direct methods and expanded using Fourier techniques<sup>[10]</sup>. The final cycle of full-matrix refinement was made using SHELXL 97<sup>[11]</sup>, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. Crystal data, data collection details and structure solution and refinement are listed in Table 1.

CCDC: 196070 for complex **2**; 186859 for complex **3**.

## 2 Results and Discussion

### 2.1 Structure Description of the Complexes

The ORTEP drawings of complex **2** and **3** are shown in Fig. 1 and Fig. 2, and the selected bond lengths and bond angles are shown in Table 2.

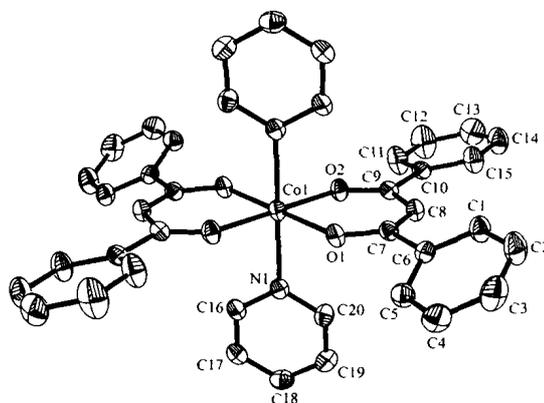


Fig. 1 ORTEP drawing of complex **2** with 30% thermal ellipsoids

The structure of complex **2** is monoclinic with a space group of  $P2_1/c$ ; and neutral molecules of  $\text{Co}(\text{DBM})_2(\text{Py})_2$  are assembled with only Van der Waals interactions. Each Co (II) atom resides on an inversion center and has a distorted octahedral environment defined by four oxygen atoms from the two DBMs and two nitrogen atoms from axial pyridines. The bond lengths of Co-O and Co-N are 2.0476(13) ~ 2.0521(13) and 2.2258(17) Å respectively and the

Table 1 Crystal Data and Structure Refinement for Complex **2** and **3**

	complex <b>2</b>	complex <b>3</b>
empirical formula	$\text{C}_{40}\text{H}_{32}\text{CoN}_2\text{O}_4$	$\text{C}_{36}\text{H}_{44}\text{CoN}_2\text{O}_4$
formula weight	663.61	867.86
temperature/K	293(2)	291(2)
wavelength/Å	0.71073	0.71073
crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
$a/\text{Å}$	8.415(2)	10.180(2)
$b/\text{Å}$	10.891(2)	19.633(4)
$c/\text{Å}$	18.191(4)	11.191(2)
$\beta/^\circ$	103.32(3)	104.35(3)
volume/ $\text{Å}^3$	1622.3(6)	2167.0(7)
Z	2	2
calculated density/ $(\text{Mg} \cdot \text{m}^{-3})$	1.358	1.330
absorption coefficient/ $\text{mm}^{-1}$	0.574	0.448
$F(000)$	690	906
crystal size/mm	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.20
$\theta$ range for data collection/ $^\circ$	2.20 to 27.53	2.07 to 27.5
reflections collected/unique	4795/2900 [ $R(\text{int}) = 0.0303$ ]	3529/3529 [ $R(\text{int}) = 0.0000$ ]
data/restraints/parameters	2900/0/215	3529/0/287
goodness-of-fit on $F^2$	1.113	1.055
final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0536$ , $wR_2 = 0.0942$	$R_1 = 0.0992$ , $wR_2 = 0.0917$
$R$ indices (all data)	$R_1 = 0.0852$ , $wR_2 = 0.1034$	$R_1 = 0.2029$ , $wR_2 = 0.1131$
extinction coefficient	0.0097(6)	0.0000(4)
largest diff. peak and hole/ $(e \cdot \text{Å}^{-3})$	0.191 and -0.343	0.341 and -0.311

Table 2 Bond Lengths(Å) and Angles(°) for Complex 2 and 3

complex 2					
Co(1)-O(1)	2.0476(13)	Co(1)-O(1)#	2.0476(13)	Co(1)-O(2)#	2.0521(13)
Co(1)-O(2)	2.0521(13)	Co(1)-N(1)	2.2258(17)	Co(1)-N(1)#	2.2258(17)
O(1)-C(7)	1.276(2)	O(2)-C(9)	1.273(2)	C(6)-C(7)	1.501(2)
C(7)-C(8)	1.397(3)	C(8)-C(9)	1.410(2)	C(9)-C(10)	1.503(3)
O(1)-Co(1)-O(1)#	180.00(4)	O(1)-Co(1)-O(2)#	92.38(5)	O(1)#-Co(1)-O(2)#	87.62(5)
O(2)#-Co(1)-O(2)	180.00(7)	O(1)-Co(1)-N(1)	88.84(6)	O(1)#-Co(1)-N(1)	91.16(6)
N(1)-Co(1)-N(1)#	180.00(10)	C(7)-O(1)-Co(1)	128.27(12)	C(9)-O(2)-Co(1)	128.75(12)
C(16)-N(1)-Co(1)	121.90(13)	C(5)-C(6)-C(7)	119.49(16)	O(1)-C(7)-C(8)	125.00(16)
O(1)-C(7)-C(6)	115.36(16)	C(7)-C(8)-C(9)	126.01(17)	C(8)-C(9)-C(10)	119.56(16)
complex 3					
Co(1)-O(1)	2.033(3)	Co(1)-O(1)#1	2.033(3)	Co(1)-O(2)#1	2.036(3)
Co(1)-O(2)	2.036(3)	Co(1)-N(1)#1	2.263(5)	Co(1)-N(1)	2.263(5)
O(1)-C(7)	1.274(5)	O(2)-C(9)	1.281(5)	N(1)-C(16)	1.327(7)
N(1)-C(20)	1.378(7)	C(7)-C(8)	1.397(7)	C(8)-C(9)	1.398(7)
O(1)-Co(1)-O(1)#1	180.0(7)	O(1)-Co(1)-O(2)#1	91.13(13)	O(1)#1-Co(1)-O(2)#1	88.87(13)
O(2)#1-Co(1)-O(2)	180.0(10)	O(1)-Co(1)-N(1)#1	87.47(15)	O(1)#1-Co(1)-N(1)#1	92.53(15)
O(2)#1-Co(1)-N(1)#1	87.90(16)	O(2)-Co(1)-N(1)#1	92.10(16)	N(1)#1-Co(1)-N(1)	180.0(2)
C(7)-O(1)-Co(1)	127.0(3)	C(9)-O(2)-Co(1)	127.7(4)	C(16)-N(1)-Co(1)	112.9(4)
C(20)-N(1)-Co(1)	130.4(4)	O(1)-C(7)-C(8)	124.8(5)	O(1)-C(7)-C(6)	115.3(5)
C(7)-C(8)-C(9)	127.0(4)	O(2)-C(9)-C(8)	123.7(5)		

#: -x, -y, -z; #1: -x, 0.5+y, 0.5-z.

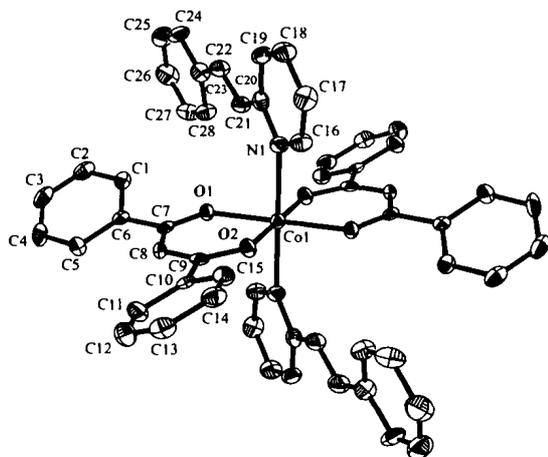


Fig. 2 ORTEP drawing of complex 3 with 30% thermal ellipsoids

coordination angles of O-Co-O and O-Co-N vary from 87.62° to 92.38°. The rotational orientations of terminal phenyl rings are dictated by both electronic and dominant steric effect. The chelate fragment is planar and the bond lengths for C(7)-O(1) [1.276(2) Å], C(9)-O(2) [1.273(2) Å], C(7)-C(8) [1.397(3) Å] and C(9)-C(8) [1.410(2) Å] imply strong conjugation in the chelate rings. The whole molecule is nearly

planar, with the average and the maximal deviations from the least square plane to be of 0.1822 and 0.5139 Å, respectively. Due to steric problems, the molecules cannot adopt ideal plane. This is avoided partially by a slight turning of the phenyl rings. The C(1)~C(6) ring bends by 29.6° and C(10)~C(15) ring rotates by 25.1° with respect to the chelate fragment. This results in the contact of H(8A)-H(1A) (2.217 Å) and H(8A)-H(15A) (2.059 Å) to be slightly shorter than the sum of hydrogen Ver der Waals radius (2.32 Å).

The crystal structure of complex 3 is very similar to that of 2. It is also centrosymmetric with a space group of  $P2_1/n$ , and the Co(II) adopts the same mode of ligand coordination. The octahedral environment of Co(II) center is more distorted owing to the bulkiness of the axial ligands. The bond lengths of Co-O and Co-N are 2.033(3) Å and 2.2263(5) Å respectively and the coordination angles of O-Co-O and O-Co-N vary from 87.47 Å to 92.53 Å.

## 2.2 Complexation and Ligands Metatheses

Cobalt (II) formed complexes with two DBM and

two other unidentate ligands in an octahedral coordination sphere, where the two DBMs were in the planar position and the two other unidentate ligands in the axial position. This coordination sphere could be easily seen from the crystal structures of  $[\text{Co}(\text{DBM})_2\text{Py}_2]$  (**2**, Py = pyridine) (Fig. 1) and  $[\text{Co}(\text{DBM})_2\text{Sbz}_2]$  (**3**, Sbz =  $\alpha$ -stilbazole) (Fig. 2). In these complexes, the dbms are not easily dissociable because of the attraction of the opposite charges and the chelating effects. But the other two unidentate ligands are easily dissociable. When complex **1** was treated with pyridine or its derivatives, the hard donor-atom ligand  $\text{H}_2\text{O}$  was replaced by the soft donor-atom ligand pyridine or its derivatives. This replacement indicated that complex **1** was not so stable as complex **2**, **3** or **4** and that the former was easy to dissociate. When the replacement occurred between complex **1** and **4**, 4'-bipyridine, the reaction was very fast because of the very low solubility of the product. Complex **4** can also be obtained by the reaction of complex **2** or **3** with **4**, 4'-bipyridine. Considering the result of elemental analysis, complex **4** should be a polymer. Attempts of getting a suitable crystal of complex **4** for X-ray diffraction analysis were all in vain.

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