

# Crystal Structures and Characterizations of Bis(1-benzoylmethyl-benzotriazole-*N*<sup>3</sup>)dichoro Metal(II) Complex: [MCl<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>CH<sub>2</sub>COPh)<sub>2</sub>] [M=Zn(II), Co(II)]

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The structures of [MCl<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>CH<sub>2</sub>COPh)<sub>2</sub>] [M=Zn(II) (**1**), Co(II) (**2**)] have been determined by X-ray crystallography. They were characterized by elemental analysis, IR spectrum, electronic spectrum and thermogravimetric-differential thermal analysis. They all crystallize in the triclinic system, space group *P* $\bar{1}$ , with lattice parameters  $a=0.9449(2)$  nm,  $b=1.1291(2)$  nm,  $c=1.3637(3)$  nm,  $\alpha=111.70(3)^\circ$ ,  $\beta=94.33(3)^\circ$ ,  $\gamma=90.97(3)^\circ$ ,  $Z=2$  for compound **1**;  $a=0.9437(2)$  nm,  $b=1.1277(2)$  nm,  $c=1.3650(3)$  nm,  $\alpha=111.76(3)^\circ$ ,  $\beta=94.50(3)^\circ$ ,  $\gamma=90.80(3)^\circ$ ,  $Z=2$  for compound **2**. The metal ions are all coordinated by two Cl<sup>-</sup> anions and two nitrogen atoms of 1-benzoylmethyl-benzotriazole ligands, forming the distorted tetrahedral geometry. The Zn—Cl and Zn—N bond lengths are 0.2209(2), 0.2210(2) nm and 0.2059(4), 0.2067(4) nm, respectively. The Co—Cl and Co—N bond lengths are 0.2215(2), 0.2222(2) nm and 0.2028(5), 0.2045(5) nm, respectively. The thermogravimetric (TG) data indicate that they are nearly similar in TG curve, and there are not structural transitions in the two compounds. They all have a high thermal stability. But, there is little difference in DTG (differential thermogravimetric) curves of those two compounds. Elemental analysis, electronic and IR spectra are in agreement with the structural data.

**Keywords** tetrahedral geometry, IR spectra, TG-DTG data, single crystal structure, triazole derivative

## Introduction

Recently, the compounds containing 1*H*-1,2,4-triazole group have attracted much interest because of their exhibiting some fungicidal activity and plant growth regulating activity,<sup>1</sup> and showing antibacterial activity against *Puccinia recondite* and roots growth regulation for cucumber.<sup>2</sup> Triazole nuclei appear frequently in the structures of various natural products and biologically active compounds, notably thiamine (vitamin B), penicillins, antibiotics such as micrococcin,<sup>3</sup> and many metabolic products of fungi and primitive marine animals, including 2-(aminoalkyl)triazole-4-carboxylic acids.<sup>4</sup> Numerous triazole and their derivatives constitute a class of compounds which have been attracting considerable attention in industry and agriculture primarily due to their significant biological activities.<sup>5</sup> Also, such compounds are increasingly being studied because of the coordination chemistry of azoles acting as ligands in transition metal compounds. Zinc is a relatively abundant element in biological organisms, and plays an essential role in a large number of enzymatic reactions.<sup>6</sup> Zinc(II) being a d<sup>10</sup> ion provides few spectroscopic signatures for the monitoring of structure, however, it can

be substituted with the d<sup>7</sup> cobalt(II) ion. The resulting cobalt(II) enzymes give characteristic visible (ligand-field) absorption spectra and often show about as much catalytic activity as the native zinc enzymes.<sup>7</sup> This is a general characteristic since the coordination chemistry of cobalt(II) is very similar to that of zinc(II) and the two metal ions also show virtually identical ionic radii. In this paper, we reported the crystal structures and the characterization of bis(1-benzoylmethyl-benzotriazole-*N*<sup>3</sup>)dichoro Zn(II) and Co(II) complexes.

## Experimental

All chemicals were obtained from commercial sources and used without further purification. Solid 1-benzoylmethyl-benzotriazole (2.4 g, 10 mmol) was dissolved in ethanol (50 mL). Zinc dichloride (ZnCl<sub>2</sub> 0.7 g, 5 mmol) or cobalt dichloride (CoCl<sub>2</sub> · 6H<sub>2</sub>O 1.2 g, 5 mmol) was added at room temperature with stirring, respectively, and the resulting solution was refluxed for 4—5 h and then cooled. The colorless precipitate for **1** or blue precipitate for **2** was formed. Upon collection by filtration, the deposit was washed with ethanol and dried for 2 d in air. The colorless crystal for **1** or the blue

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crystal for **2** was obtained from ethanol. The crystals were all collected, dried and submitted for elemental analysis [Anal. calcd for  $C_{28}H_{22}Cl_2N_6O_2Zn$  (**1**): C 55.06, H 3.63, N 1.38; found C 54.83, H 3.90, N 1.33. Anal. calcd for  $C_{28}H_{22}Cl_2N_6O_2Co$  (**2**): C 55.65, H 3.67, N 1.39; found C 55.41, H 3.94, N 1.35].

Elemental analysis for carbon, hydrogen and nitrogen was performed on a Perkin-Elmer 240C analysis instrument. Solid state electronic spectra were measured on a Shimadzu UV-200 recording spectrophotometer, furnished with a reflectance attachment using  $BaSO_4$  as the reference sample. IR spectra were recorded in the range of  $4000-300\text{ cm}^{-1}$  on a Perkin-Elmer 467 spectrometer using KBr pellets. Thermogravimetry (TG) and differential thermogravimetry (DTA) were recorded on a SDT 2980 simultaneously for the samples of *ca.* 10 mg under a nitrogen atmosphere (150 mL/min) at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$ .

The summary of the key crystallographic information for these two compounds is given in Table 1. Reflection data and reflections for the unit cell determination were measured at  $20\text{ }^\circ\text{C}$  using Mo  $K\alpha$  radiation ( $\lambda=0.071073\text{ nm}$ ) with a graphite monochromator. The technique used was  $\omega$ -scan with  $\theta$  limits  $1.61^\circ < \theta < 24.98^\circ$  for the two title compounds. Empirical absorp-

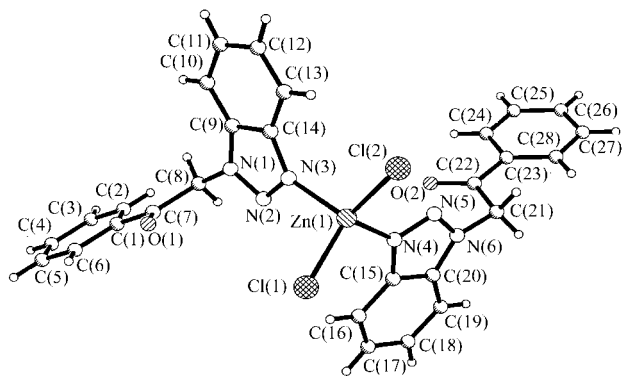
tion correction was carried out by using the SADABS<sup>8</sup> program. Both the structures of  $[ZnCl_2(C_6H_4N_3CH_2CO-Ph)_2]$  (**1**), and  $[CoCl_2(C_6H_4N_3CH_2CO-Ph)_2]$  (**2**), were solved by direct methods and refined by least squares on  $F_{obs}^2$  by using the SHELXTL<sup>9</sup> software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. For **1**, final conventional  $R(F)=0.0453$  and  $wR(F^2)=0.0918$  for  $I > 2\sigma(I)$  with weighting scheme,  $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.4269P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . For **2**, the corresponding  $R(F) = 0.0580$  and  $wR(F^2) = 0.0785$  for  $I > 2\sigma(I)$  with weighting scheme,  $w = 1/[\sigma^2(F_o^2) + (0.0185P)^2 + 0.0000P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray crystallography.<sup>10</sup>

## Results and discussion

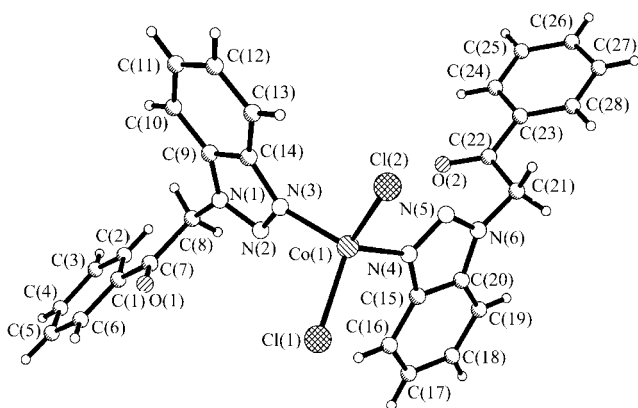
The molecular structures of compounds **1** and **2** are illustrated in Figures 1 and 2, respectively. Figure 3 shows a perspective view of the crystal packing in the unit cell for **1**. The final position parameters of non-

**Table 1** Crystal data and structure refinement for the title compounds **1** and **2**

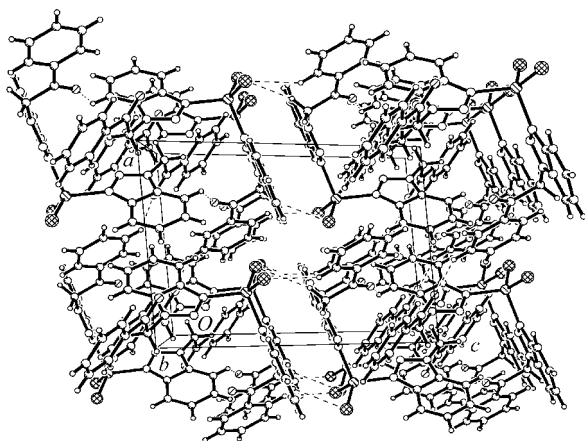
Compound	<b>1</b>	<b>2</b>
Formula	$C_{28}H_{22}Cl_2N_6O_2Zn$	$C_{28}H_{22}Cl_2N_6O_2Co$
Formula weight	610.79	604.35
Temperature/K	293(2)	293(2)
Wavelength/nm	0.071073	0.071073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions/[nm, ( $^\circ$ )]	$a=0.9449(2)$ , $\alpha=111.70(3)$ $b=1.1291(2)$ , $\beta=94.33(3)$ $c=1.3637(3)$ , $\gamma=90.97(3)$	$a=0.9437(2)$ , $\alpha=111.76(3)$ $b=1.1277(2)$ , $\beta=94.50(3)$ $c=1.3650(3)$ , $\gamma=90.80(3)$
Volume/nm <sup>3</sup>	1.3464(5)	1.3435(5)
Z, Calculated density/(Mg $\cdot$ m <sup>-3</sup> )	2, 1.507	2, 1.494
Absorption coefficient/mm <sup>-1</sup>	1.149	0.876
$F(000)$	628	622
Crystal size/mm <sup>3</sup>	$0.50 \times 0.12 \times 0.02$	$0.20 \times 0.14 \times 0.08$
$\theta$ range for data collection/ $^\circ$	1.61 to 24.98	1.61 to 24.98
Limiting indices	$0 \leq h \leq 11$ , $-13 \leq k \leq 13$ , $-16 \leq l \leq 16$	$0 \leq h \leq 11$ , $-13 \leq k \leq 13$ , $-16 \leq l \leq 16$
Reflections collected/unique	5045/4729 [ $R_{int}=0.0358$ ]	5042/4726 [ $R_{int}=0.0607$ ]
Completeness to $\theta=24.98^\circ$	99.9%	100.0%
Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraint/parameter	4729/0/352	4726/0/352
Goodness-of-fit on $F^{-2}$	1.047	0.953
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.0453$ , $wR_2=0.0918$	$R_1=0.0580$ , $wR_2=0.0785$
$R$ indices (all data)	$R_1=0.1188$ , $wR_2=0.1096$	$R_1=0.2078$ , $wR_2=0.1048$
Largest diff. peak and hole/( $e \cdot \text{nm}^{-3}$ )	408 and $-354$	396 and $-467$



**Figure 1** Molecular structure for  $[\text{ZnCl}_2(\text{C}_6\text{H}_4\text{N}_3\text{CH}_2\text{COPh})_2]$  with the atomic numbering scheme.



**Figure 2** Molecular structure for  $[\text{CoCl}_2(\text{C}_6\text{H}_4\text{N}_3\text{CH}_2\text{COPh})_2]$  with the atomic numbering scheme.



**Figure 3** Packing diagram of the unit cell of **1**.

hydrogen atoms are given in Tables 2 and 3. Selected bond distances and angles of **1** and **2** are listed in Tables 4 and 5. The two title compounds,  $[\text{MCl}_2(\text{C}_6\text{H}_4\text{N}_3\text{CH}_2\text{COPh})_2]$ , where  $\text{M}=\text{Zn}(\text{II})$  and  $\text{Co}(\text{II})$ , are isomorphous. The central metal atoms are coordinated to two  $\text{Cl}^-$  anions and two 1-benzoylmethyl-benzotriazole ligands. The environments surrounding the metal atoms are the distorted tetrahedron. In both complexes, the

**Table 2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{nm}^2 \times 10^5$ ) for the compound **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Zn(1)	2577(1)	6220(1)	8164(1)	36(1)
Cl(1)	3256(1)	8264(1)	8865(1)	49(1)
Cl(2)	3821(2)	4782(1)	8545(1)	50(1)
O(1)	2345(4)	8218(3)	5129(3)	54(1)
O(2)	-2765(4)	3802(3)	7196(3)	49(1)
N(1)	1398(4)	5968(4)	5143(3)	40(1)
N(2)	1401(4)	6420(4)	6196(3)	42(1)
N(3)	2291(4)	5764(4)	6552(3)	40(1)
N(4)	548(4)	6058(4)	8587(3)	36(1)
N(5)	88(4)	4966(4)	8626(3)	40(1)
N(6)	-1208(4)	5132(4)	8964(3)	36(1)
C(1)	550(6)	8425(5)	3883(4)	45(1)
C(2)	-672(6)	7898(5)	3224(4)	54(2)
C(3)	-1277(7)	8490(7)	2581(5)	78(2)
C(4)	-676(9)	9604(8)	2596(6)	88(2)
C(5)	534(9)	10153(7)	3245(6)	81(2)
C(6)	1145(6)	9562(5)	3891(5)	56(2)
C(7)	1273(6)	7808(5)	4573(4)	40(1)
C(8)	547(5)	6562(5)	4537(4)	44(1)
C(9)	2294(5)	4991(4)	4792(4)	35(1)
C(10)	2634(6)	4192(5)	3789(4)	51(2)
C(11)	3587(7)	3298(6)	3777(4)	66(2)
C(12)	4216(7)	3185(6)	4708(4)	68(2)
C(13)	3876(6)	3959(5)	5688(4)	53(2)
C(14)	2878(5)	4872(5)	5724(4)	38(1)
C(15)	-475(5)	6938(5)	8906(4)	34(1)
C(16)	-514(6)	8201(5)	8978(4)	49(1)
C(17)	-1736(6)	8803(5)	9295(5)	64(2)
C(18)	-2884(6)	8191(6)	9533(5)	67(2)
C(19)	-2871(6)	6954(5)	9460(4)	54(2)
C(20)	-1628(5)	6338(5)	9137(3)	34(1)
C(21)	-2042(5)	4034(5)	8955(4)	41(1)
C(22)	-2876(5)	3364(4)	7882(4)	34(1)
C(23)	-3740(5)	2190(4)	7702(4)	34(1)
C(24)	-4478(5)	1574(5)	6714(4)	43(1)
C(25)	-5278(6)	483(5)	6517(4)	52(2)
C(26)	-5363(6)	-20(5)	7290(4)	52(2)
C(27)	-4624(6)	570(5)	8259(4)	56(2)
C(28)	-3824(6)	1673(5)	8475(4)	47(1)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 3** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{nm}^2 \times 10^5$ ) for the compound **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Co(1)	12523(1)	6206(1)	3139(1)	37(1)	C(9)	12294(7)	4999(6)	-215(5)	34(2)
Cl(1)	13252(2)	8247(2)	3853(1)	51(1)	C(8)	10544(6)	6565(6)	-483(5)	42(2)
Cl(2)	13804(2)	4780(2)	3535(1)	53(1)	C(7)	11264(7)	7814(6)	-437(5)	40(2)
O(1)	12349(5)	8226(4)	132(4)	54(1)	C(1)	10544(7)	8438(6)	-1118(5)	40(2)
O(2)	7226(5)	3803(4)	2204(3)	48(1)	C(2)	9324(7)	7912(6)	-1792(5)	51(2)
N(1)	11381(5)	5967(5)	132(4)	36(1)	C(3)	8718(9)	8501(8)	-2431(6)	75(3)
N(2)	11385(5)	6418(5)	1187(4)	41(2)	C(4)	9322(10)	9638(9)	-2383(8)	92(3)
N(3)	12268(5)	5764(5)	1552(4)	39(1)	C(5)	10542(10)	10161(8)	-1734(7)	78(3)
N(6)	8776(5)	5128(5)	3976(4)	37(1)	C(6)	11146(8)	9575(7)	-1095(6)	59(2)
N(5)	10082(6)	4956(5)	3627(4)	41(1)	C(15)	9523(6)	6936(6)	3913(5)	34(2)
N(4)	10542(5)	6045(5)	3600(4)	34(1)	C(16)	9473(7)	8200(6)	3983(5)	49(2)
C(14)	12876(6)	4880(6)	715(4)	32(2)	C(17)	8256(8)	8797(7)	4307(6)	67(2)
C(13)	13869(7)	3963(6)	694(5)	47(2)	C(18)	7105(8)	8187(8)	4548(6)	72(2)
C(12)	14209(8)	3196(7)	-281(6)	64(2)	C(19)	7121(7)	6944(7)	4470(5)	54(2)
C(11)	13614(8)	3305(7)	-1220(6)	67(2)	C(20)	8373(7)	6351(6)	4154(5)	32(2)
C(10)	12654(7)	4199(7)	-1207(5)	50(2)					

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 4** Selected bond lengths (nm) and angles ( $^\circ$ ) for compound **1**

Zn(1)—N(3)	0.2059(4)	Zn(1)—N(4)	0.2068(4)
Zn(1)—Cl(1)	0.2209(2)	Zn(1)—Cl(2)	0.2210(2)
O(1)—C(7)	0.1193(6)	O(2)—C(22)	0.1221(5)
N(3)—Zn(1)—N(4)	103.92(16)	N(3)—Zn(1)—Cl(1)	106.21(12)
N(4)—Zn(1)—Cl(1)	106.96(12)	N(3)—Zn(1)—Cl(2)	110.93(13)
N(4)—Zn(1)—Cl(2)	106.67(12)	Cl(1)—Zn(1)—Cl(2)	120.85(6)
N(2)—N(1)—C(9)	110.5(4)	O(1)—C(7)—C(1)	124.4(5)
O(1)—C(7)—C(8)	119.8(5)	O(2)—C(22)—C(23)	122.6(4)
O(2)—C(22)—C(21)	118.4(4)		

**Table 5** Selected bond lengths (nm) and angles ( $^\circ$ ) for compound **2**

Co(1)—N(3)	0.2029(5)	Co(1)—N(4)	0.2046(5)
Co(1)—Cl(1)	0.2215(2)	Co(1)—Cl(2)	0.2222(2)
O(1)—C(7)	0.1211(7)	O(2)—C(22)	0.1207(6)
N(3)—Co(1)—N(4)	106.6(2)	N(3)—Co(1)—Cl(1)	106.26(16)
N(4)—Co(1)—Cl(1)	107.67(16)	N(3)—Co(1)—Cl(2)	110.87(17)
N(4)—Co(1)—Cl(2)	105.99(16)	Cl(1)—Co(1)—Cl(2)	118.81(8)
O(1)—C(7)—C(1)	124.4(6)	O(1)—C(7)—C(8)	119.4(6)
O(2)—C(22)—C(23)	123.3(6)	O(2)—C(22)—C(21)	118.5(6)

benzotriazole ring 1 [N(1), N(2), N(3), C(9), C(10), C(11), C(12), C(13) and C(14)] is fairly planar with the conjunction carbon atom C(8) and M atom, and the de-

viation from the least squares plane through the ring atoms is 0.0041 nm for these two compounds. The phenyl ring 3 [C(1), C(2), C(3), C(4), C(5) and C(6)] is quite planar with the conjunction carbonyl group C(7) and O(1), and the largest deviation from the least squares plane is 0.0027 nm for **1** and 0.0025 nm for **2**, respectively. The dihedral angles between the benzotriazole ring 1 and the phenyl ring 3 are  $76.61^\circ$  for **1** and  $76.53^\circ$  for **2**, respectively. The benzotriazole ring 2 [N(4), N(5), N(6), C(15), C(16), C(17), C(18), C(19) and C(20)] is fairly planar with the M atom, with a maximum deviation of the same 0.0024 nm for these two compounds. The phenyl ring 4 [C(23), C(24), C(25), C(26), C(27) and C(28)] is quite planar with the conjunction acetyl [C(21), C(22) and O(2)] and the N(6) atom from the benzotriazole ring 2, and the largest deviation from the least squares plane is 0.0025 nm for **1** and 0.0026 nm for **2**, respectively. The dihedral angles between the plane of benzotriazole ring 2 and the plane of phenyl ring 4 are  $88.76^\circ$  for **1** and  $89.08^\circ$  for **2**, respectively.

In the compound **1**, the average Zn—Cl distance of 0.2209 nm is shorter than the corresponding average distances reported for related metal complexes with distorted  $\text{ZnN}_2\text{Cl}_2$  tetrahedral environments,<sup>11</sup> but comparable to 0.2212(4) nm in  $\text{ZnCl}_2(2,9\text{-dimethyl-1,10-phenanthroline})$ <sup>12</sup> and 0.2209(3) nm in  $\text{ZnCl}_2(4\text{-vinylpyridine})_2$ .<sup>13</sup> The average Zn—N bond distance of 0.2063(4) nm is comparable to reported average values,<sup>11d,14</sup> but longer than the average value of 0.2039(3) nm in  $\text{ZnCl}_2(5,7\text{-dimethyl-1,2,4-triazolo}[1,5-\alpha]\text{pyrimidine})_2$ ,<sup>11a</sup> 0.2027(3) nm in  $\text{ZnCl}_2[1\text{-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-thiopropyl}]$ <sup>11b</sup> and

0.2007(4) nm in  $Zn_{0.99}Cu_{0.01}Cl_2(1,2\text{-dimethyl imidazole})_2$ .<sup>15</sup>

In the compound **2**, the Co—Cl distances of 0.2215(2) and 0.2222(2) nm are comparable with the corresponding values in the reported complex  $Co(\text{imidazole})_2Cl_2$  [0.224(1) and 0.226(1) nm]<sup>16</sup> and  $Co(\text{bdmpab})Cl_2$  [0.22434(8) nm and 0.22266(8) nm;  $\text{bdmpab} = N,N\text{-bis}(3,5\text{-dimethylpyrazol-1-ylmethyl})\text{aminobenzene}$ ].<sup>17</sup> The Co—N distances of 0.2028(5) nm and 0.2045(4) nm are shorter than those of truly six-coordinate cobalt(II) complex,<sup>18</sup> but little longer than that of square-planar cobalt(II) complex with  $CoN_4$  core [average 0.1875 nm],<sup>19</sup> but are comparable with those of the tetrahedral cobalt(II) complex,  $Co(\text{bdmpab})Cl_2$ , [0.2038(2) and 0.2044(2) nm].<sup>17</sup>

The two compounds have a similar structure. There are some intermolecular interactions (C—H $\cdots$ Y hydrogen bonds, Y=O and Cl)<sup>20</sup> in two lattice structures. The donor and acceptor distances are C(10) $\cdots$ O(2) 0.30347 nm [symmetry code:  $-x, 1-y, 1-z$ ]; C(21) $\cdots$ Cl(2) 0.37159 nm [symmetry code:  $-x, 1-y, -z$ ]; C(25) $\cdots$ O(1) 0.32789 nm [symmetry code:  $1+x, 1+y, z$ ] for compound **1** and C(10) $\cdots$ O(2) 0.30377 nm [symmetry code:  $2-x, 1-y, -z$ ]; C(25) $\cdots$ O(1) 0.32507 nm [symmetry code:  $-1+x, -1+y, z$ ]; C(21) $\cdots$ Cl(2) 0.37160 nm [symmetry code:  $2-x, 1-y, 1-z$ ] for compound **2** respectively. These intermolecular hydrogen bonds link the molecules into two-dimensional hydrogen bond networks which stabilize the crystal structure.

The IR spectra of the compounds **1** and **2** show a little difference. The broad absorptions at  $3434\text{ cm}^{-1}$  for **1** and at  $3444\text{ cm}^{-1}$  for **2** are assigned to the C—H stretching vibration of the benzotriazole ring. The strong bands at  $1696\text{ cm}^{-1}$  in **1** and at  $1694\text{ cm}^{-1}$  in **2** are assigned to the stretching vibration of  $\nu_{C=O}$  of PhCO. They all exhibit characteristic strong bands at 1596 (C=C), 1451, 1328 (C=N), 827 ( $\nu_{C-H}$  benzene ring) and  $750\text{ cm}^{-1}$  ( $\nu_{C-H}$  triazole ring) for the coordinate benzotriazole ligands.<sup>21</sup> The bands at 1451 and  $1328\text{ cm}^{-1}$  are shifted from their positions for the free benzotriazole ligand ( $1454$  and  $1383\text{ cm}^{-1}$ ),<sup>22</sup> indicating nitrogen coordination.

The solid reflectance electronic spectrum of compound **1** shows two broad bands around 250 and 301 nm. The band around 250 nm is ascribed to intra-ligand, probably  $\pi \rightarrow \pi^*$ , transition of the benzotriazolyl group. The peak at 301 nm may be responsible for ligand to metal charge transfer (LMCT).<sup>21</sup> The compound **2** shows five broad bands around 243, 322, 479, 511 and 583 nm. The band around 243 nm is also ascribed to intra-ligand transition of the benzotriazolyl group and the band around 322 nm to metal charge transfer. The band at 479, 511 and 583 nm are d-d transfer transitions of Co(II), which may be taken as evidence for tetrahedral Co(II) complexes.<sup>23</sup>

Thermal analysis curves of the title compounds **1** and **2** are shown in Figures 4 and 5, respectively. They are little different in DTG curves. In compound **1**, there

are two endothermic peaks, one intense heat-absorbing peak at  $287.4\text{ }^\circ\text{C}$  and one very weak peak at  $616.1\text{ }^\circ\text{C}$ . It shows no decomposition before  $285\text{ }^\circ\text{C}$ ; but, at  $287\text{ }^\circ\text{C}$ , decomposition occurs. On the base of weight changes in the TG curve, the first process of the weight loss (25.35%) corresponds to the loss of phenyl ring (found 25.35%, calcd 25.18%), with an intense endothermic phenomenon; then, the decomposition continues. The weight of the residue 5.75%, which is smaller than that of the residual Zn (10.66%), suggests that there were some residue sublimations. In compound **2**, there are several exothermic peaks and endothermic peaks. From the Figure 5, we can see that there are four steps of weight loss. There is one intense endothermic peak in the DTG curve at  $271.6\text{ }^\circ\text{C}$ , and about 25.55% weight loss in the TG curve between  $270\text{--}300\text{ }^\circ\text{C}$ , which is also attributed to the loss of phenyl ring (found 25.55% calcd 25.43%). Then, the second event of the weight loss may be related to the loss of ethyl carbonyl ( $\text{CH}_2\text{CO}$ ) (found 41.36%, calcd 39.30%). Finally, the weight loss of 91.41% suggests that the residue may be Co atom (found 8.59%, calcd 9.73%). Meanwhile, no structural transitions were found in these two compounds, which imply a high thermal stability of them.

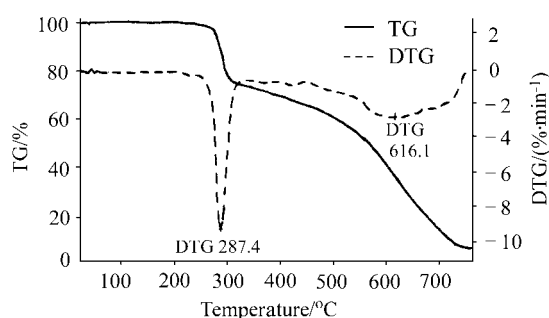


Figure 4 TG/DTG curves of compound **1**.

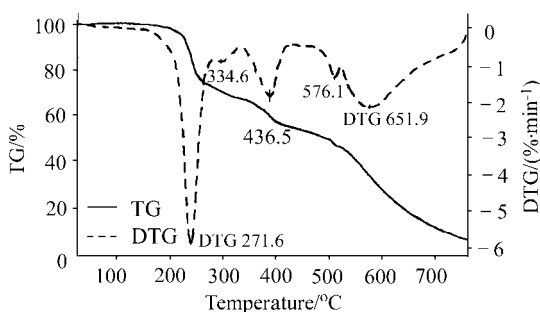


Figure 5 TG/DTG curves of compound **2**.

## References

- Zhou, Z. H.; Zhao, J.; Peng, Y. B.; Zhao, G. F. *Appl. Chem.* **1998**, *15*, 72 (in Chinese).
- Zhao, J.; Zhou, Z. Z.; Peng, Y. B.; Zhao, G. F. *Huaxue Tongbao* **1998**, (8), 35 (in Chinese).
- James, M. N. G.; Watson, K. J. *J. Chem. Soc. C* **1966**, 1361.
- Schmidt, U.; Utz, R.; Lieberknecht, A.; Griesser, H.; Pot-

- zolli, B.; Bahr, J.; Wagner, K.; Fischer, P. *Synthesis* **1987**, 233.
- 5 (a) Zhang, Y.; Sun, X. W.; Hui, X. P.; Zhang, Z. X.; Wang, Q.; Zhang, Q. *Chin. J. Chem.* **2002**, *20*, 168.  
(b) Pujar, M. A.; Bharamgoudar, T. D.; Sathyanarayana, D. N. *Transition Met. Chem.* **1988**, *13*, 423.  
(c) Bouwman, E.; Driessen, W. L.; Reedijk, J. *Coord. Chem. Rev.* **1990**, *104*, 143.
- 6 Liljas, A.; Kannan, K. K.; Bergsten, P. C.; Waara, I.; Fridborg, K.; Strandberg, B.; Carlbom, U.; Jarup, L.; Lovgren, S.; Petef, M. *Nature (London) New Biol.* **1972**, *235*(57), 131.
- 7 Vallee, B. L.; Riordan, J. F.; Johanson, J. T.; Livingston, D. M. *Cold Spring Harbor Symp. Quant. Biol.* **1971**, *36*, 517.
- 8 Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1969**, *46*, 467.
- 9 Sheldrick, G. M. *SHELXTL97*, Program for Crystal Structure refinement, University of Gottingen, Germany, **1993**.
- 10 Wilson, A. J. *International Table for X-ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, **1992**, Tables 6.1.1.4 (pp. 500—502) and 4.2.6.8 (pp. 219—222).
- 11 (a) Salas, J. M.; Romero, M. A.; Rahmani, A. *Acta Crystallogr.* **1994**, *C50*, 510.  
(b) Matthews, C. J.; Clegg, W.; Heath, S. L.; Martin, N. C.; Hill, S. M. N.; Lockhart, J. C. *Inorg. Chem. Rev.* **1998**, *37*, 199.  
(c) Laity, H. L.; Taylor, M. R. *Acta Crystallogr.* **1995**, *C51*, 1791.  
(d) Bei, F. L.; Jian, F. F.; Yang, X. J.; Lu, L. D.; Wang, X.; Razak, I. A.; Raj, S. S. S.; Fun, H. K. *Acta Crystallogr.* **2001**, *C57*, 45.
- 12 Preston, H. S.; Dennard, C. H. L. *J. Chem. Soc. A* **1969**, 1956.
- 13 Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 1119.
- 14 (a) Baenziger, N. C.; Schultz, R. *J. Inorg. Chem.* **1971**, *10*, 661.  
(b) Beauchamp, A. L. *Inorg. Chim. Acta* **1984**, *91*, 33.
- 15 Bharadwaj, P. K.; Schugar, H. J.; Potenza, J. A. *Acta Crystallogr.* **1991**, *C47*, 754.
- 16 Laing, M.; Carr, G. *Acta Crystallogr.* **1975**, *C31*, 2683.
- 17 Blonk, H. L.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1699.
- 18 (a) Sun, W. Y.; Fei, B. L.; Okamura, T. A.; Zhang, Y. A.; Ye, T.; Tang, W. X.; Ueyama, N. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2733.  
(b) Li, J. M.; Zhang, Y. G.; Lin, W. B.; Liu, S. X.; Huang, J. L. *Polyhedron* **1992**, *11*, 419.  
(c) Wang, Z. X.; Jian, F. F.; Zhang, Y. R.; Li, F. S.; Fun, H. K.; Chinnakali, K. J. *Chem. Crystallogr.* **1999**, *29*, 885.
- 19 Jaynes, B. S.; Doerrer, L. H.; Liu, S.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5735.
- 20 (a) Steiner, T. *Crystallogr. Rev.* **1996**, *6*, 1.  
(b) Jeffrey, G. A.; Maluszynska, H.; Mitra J. *Int. J. Biol. Macromol.* **1985**, *7*, 336.
- 21 Liao, Z. R.; Xiang, D. F.; Li, D. F.; Mei, F. S.; Xiong, Y. *Synth. React. Inorg. Met.-Org. Chem.*, **1998**, *28*, 1327.
- 22 Socrates, G. *Infrared Characteristic Group Frequencies*, John Wiley & Sons, Chichester, New York, **1989**.
- 23 Zhao, H. B.; Cai, J.; Lin, Y. B.; Luo, Z. Q.; Liu, J.; Ning, J. H.; Zhou, J. H. *Chin. J. Inorg. Chem.* **2000**, *16*, 515 (in Chinese).

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