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Synthesis of 1-substituted benzimidazole metal complexes and structural characterization of dichlorobis(1-phenyl-1 H benzimidazole-  $\kappa N^{-3}$ )cobalt(II) and dichlorobis (1-phenyl-1 H benzimidazole-  $\kappa N^{-3}$ )zinc(II)

Nıhat Şırecı<sup>a</sup>, Ülkü Yilmaz<sup>b</sup>, Hasan Küçükbay<sup>ab</sup>, Mehmet Akkurt<sup>c</sup>, Zelıha Baktir<sup>c</sup>, Sevım Türktekın<sup>c</sup> & Orhan Büyükgüngör <sup>d</sup>

 $^{\rm a}$  Faculty of Education , Adıyaman University , 02040 Adıyaman , Turkey

<sup>b</sup> Department of Chemistry, Faculty of Arts and Sciences , 1nönü University , 44280 Malatya , Turkey

<sup>c</sup> Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey

<sup>d</sup> Department of Physics, Faculty of Arts and Sciences , Ondokuz Mayis University , 55139 Samsun , Turkey Published online: 23 May 2011.

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# Synthesis of 1-substituted benzimidazole metal complexes and structural characterization of dichlorobis(1-phenyl-1H-benzimidazole- $\kappa N^3$ )cobalt(II) and dichlorobis (1-phenyl-1H-benzimidazole- $\kappa N^3$ )zinc(II)

NİHAT ŞİREC݆, ÜLKÜ YILMAZ‡, HASAN KÜÇÜKBAY\*‡, MEHMET AKKURT§, ZELİHA BAKTIR§, SEVİM TÜRKTEKİN§ and ORHAN BÜYÜKGÜNGÖR¶

†Faculty of Education, Adıyaman University, 02040 Adıyaman, Turkey
‡Department of Chemistry, Faculty of Arts and Sciences, İnönü University, 44280 Malatya, Turkey
§Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey
¶Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Samsun, Turkey

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The Co(II), Zn(II), Ni(II), Cu(II), and Fe(II) complexes of 1-phenylbenzimidazole were synthesized and characterized by NMR and elemental analyses. The crystal structures of dichlorobis(1-phenyl-1 *H*-benzimidazole- $\kappa N^3$ )cobalt(II) and dichlorobis(1-phenyl-1 *H*-benzimidazole- $\kappa N^3$ )cinc(II) have been determined by single-crystal X-ray diffraction.

*Keywords*: Benzimidazole metal complexes; Transition metal complexes; Coordination compounds; Crystal structure

#### 1. Introduction

Nitrogen-containing heterocyclic compounds play an important role in biological systems and in many industrial fields. Benzimidazoles display a wide range of pharmacological activities, and are used for therapeutic purposes as antifungal, antibacterial, antihelmintic, hypotensive, vasodilator, spasmolytic, and antiulcer activities. In addition to their biological importance, benzimidazoles form stable complexes with various transition metals [1]. The transition metal complexes of benzimidazoles are used to model important bioinorganic systems due to their promising therapeutic potential [2–4]; most works carried out on these classes of compounds are connected with their medicinal properties [5–7]. If the ring substituents change, the electron distribution and coordination ability are affected [8, 9].

<sup>\*</sup>Corresponding author. Email: hkucukbay@inonu.edu.tr

There are many reports of benzimidazole transition metal complexes including mono-, bi-, and tri-dentate benzimidazoles. Some consist of 2-substituted benzimidazole and the others consist of benzimidazole-based mixed ligands [10–14]. Recently, we reported on the structural and chemical properties of some trimethylsilyl-substituted benzimidazole derivatives [15, 16].

Most of the studies utilize alkyl-substituted benzimidazole; there is no example containing 1-phenyl-substituted benzimidazole metal complex in the literature. For this reason, we focused on the synthesis and characterization of 1-aryl-substituted benzimidazole-based transition metal complexes.

We report herein the preparation and characterization of cobalt(II), zinc(II), nickel(II), copper(II), and iron(II) coordination compounds with 1-phenylbenzimidazole. The crystal structures of dichlorobis(1-phenylbenzimidazole-1 *H*-benzimidazole- $\kappa N^3$ )cobalt(II) (1) and dichlorobis(1-phenylbenzimidazole-1 *H*-benzimidazole- $\kappa N^3$ )zinc(II) (2) were determined by single-crystal X-ray diffraction.

### 2. Experimental

All preparations were carried out in an atmosphere of purified argon using standard Schlenk techniques. Starting materials and reagents used in reactions were supplied commercially from Aldrich or Merck Chemical Co. Solvents were dried according to standard methods and freshly distilled prior to use. <sup>1</sup>H-NMR (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra were recorded using a Bruker DPX-300 high performance digital FT NMR spectrometer. Because of the paramagnetic cobalt, nickel, copper, and iron, <sup>1</sup>H-NMR spectra of these complexes were recorded as broad peaks through diluted sample solutions with doubling of scans. Infrared (IR) spectra were recorded using an ATR unit from 4000 to 200 cm<sup>-1</sup> on a Perkin-Elmer FT-IR spectrophotometer. Elemental analyses were performed with a LECO CHNS-932 elemental analyzer at the Scientific and Technological Research Centre of İnönü University (Malatya-Turkey). UV-Vis spectra were measured on a Perkin-Elmer Lambda 35 spectrophotometer. Melting points were recorded using an electrothermal-9200 melting point apparatus and are uncorrected. Magnetic measurements were carried out on a Sherwood Scientific apparatus at room temperature by Gouy's method using  $CuSO_4 \cdot 5H_2O$  as calibrant corrected and were for diamagnetism by applying Pascal's constants. 1-Phenylbenzimidazole was synthesized according to the literature procedure [17, 18]. Compounds 1–5 were synthesized from 1-phenylbenzimidazole with cobalt(II), zinc(II), nickel(II), copper(II), and iron(II) chloride in DMF (scheme 1).

# 2.1. Preparation of dichlorobis(1-phenylbenzimidazole-1 H-benzimidazole- $\kappa N^3$ )cobalt(II) (1)

A solution of 1-phenylbenzimidazole (1.75 g, 9.00 mmol) and cobalt(II) chloride (0.58 g, 4.50 mmol) in DMF ( $4 \text{ cm}^3$ ) was heated under reflux for 2 h. The mixture was then cooled to room temperature, after which solvent was removed from the filtrate *in vacuo*. The precipitate was then crystallized from EtOH/DMF (2:1). Yield: 2.06 g (88%); m.p.:



Scheme 1. Synthesis of 1-phenylbenzimidazoles metal complexes.

207–208°C. Anal. Calcd for C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>CoCl<sub>2</sub> (%): C, 60.25; H, 3.89; N, 10.81. Found (%): C, 60.21; H, 3.85; N, 10.80.  $\nu_{(N=C)}$ : 1481 cm<sup>-1</sup>.

Similarly, 2–5 were obtained by the reaction of 1-phenylbenzimidazole with zinc chloride, nickel chloride, copper chloride, and iron chloride, respectively.

## **2.2.** Dichlorobis(1-phenylbenzimidazole-1 H-benzimidazole- $\kappa N^3$ )zinc(II) (2)

Yield: 2.16 g, 91%; m.p.: 223–224°C. Anal. Calcd for  $C_{26}H_{20}N_4ZnCl_2$  (%): C, 59.51; H, 3.84; N, 10.68. Found (%): C, 59.45; H, 3.82; N, 10.63.  $\nu_{(N=C)}$ : 1481 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.74 (s, 2 H, NC*H*N), 7.97–7.37 (m, 18 H, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  144.1 (NCHN), 142.6, 135.9, 133.4, 130.6, 128.8, 124.6, 123.6, 119.9, 111.5 ( $C_6H_4$  and  $C_6H_5$ ).

# **2.3.** Dichlorobis(1-phenylbenzimidazole-1 H-benzimidazole- $\kappa N^3$ )nickel(II) (3)

Yield: 1.99 g, 85%; m.p.: 102–103°C. Anal. Calcd for  $C_{26}H_{20}N_4NiCl_2$  (%): C, 60.28; H, 3.89; N, 10.81. Found (%): C, 60.24; H, 3.88; N, 10.80.  $\nu_{(N=C)}$ : 1481 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.12 (br s, 2 H, NCHN), 7.77–7.03 (m, 18 H, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>).

# **2.4.** Dichlorobis(1-phenylbenzimidazole-1 H-benzimidazole- $\kappa N^3$ ) copper(II) (4)

Yield: 2.13 g, 90%; m.p.: 209–210°C. Anal. Calcd for  $C_{26}H_{20}N_4CuCl_2$  (%): C, 59.72; H, 3.86; N, 10.71. Found (%): C, 59.61; H, 3.81; N, 10.62.  $\nu_{(N=C)}$ : 1481 cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\delta$ , DMSO-d<sub>6</sub>):  $\delta$  8.00 (br s, 2 H, NCHN), 7.70–6.69 (m, 18 H, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>).

## **2.5.** Dichlorobis(1-phenylbenzimidazole-1 H-benzimidazole- $\kappa N^3$ )iron(II) (5)

Yield: 2.02 g, 87%; m.p.: 217–218°C. Anal. Calcd for  $C_{26}H_{20}N_4FeCl_2$  (%): C, 60.61; H, 3.91; N, 10.87. Found (%): C, 60.58; H, 3.86; N, 10.83.  $\nu_{(N=C)}$ : 1480 cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\delta$ , DMSO-d<sub>6</sub>):  $\delta$  8.64 (br s, 2 H, NCHN), 7.20–7.80 (m, 18 H, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>).



Figure 1. (a) View of 1, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. (Symmetry code: (a) 1-x, y, 1-z). (b) View of 2, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

#### 2.6. Crystal structure determinations of 1 and 2

Crystallographic data for **1** and **2** were collected at 296(2) K on a STOE IPDS 2 diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å); crystal structures were solved by direct methods using SIR97 structure solution program [19]. Refinement was performed by the difference-Fourier method of SHELXL97 [20]. All hydrogens were positioned geometrically and refined using a riding model. ORTEP [21] representations of **1** and **2** are in figure 1(a) and (b). Table 1 lists cell information, data collection parameters, and refinement data. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographic data and structure refinements for 1 and 2.

Compound	1	2
Empirical formula	C <sub>26</sub> H <sub>20</sub> Cl <sub>2</sub> CoN <sub>4</sub>	$C_{26}H_{20}Cl_2N_4Zn$
Formula weight	518.29	524.75
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	C2	$P\bar{1}$
Unit cell dimensions (Å, °)	Cell parameters from	Cell parameters from
a	20.0470(12)	7 3346(5)
h	6 0254(2)	10 1589(7)
c	12.1069(7)	16.9840(11)
α	_	77.161(5)
β	126.060(4)	85.537(5)
γ	_	78.869(5)
Volume (Å <sup>3</sup> ), Z	1182.21(12), 2	1209.85(14), 2
Calculated density, $D_x$ (Mg m <sup>-3</sup> )	1.456	1.441
Absorption coefficient $(mm^{-1})$	0.97	1.26
Crystal size (mm <sup>3</sup> )	$0.52 \times 0.62 \times 0.68$	$0.24 \times 0.38 \times 0.62$
F(000)	530	536
$\theta$ range (°)	2.1-28.0	2.1-27.2
Number of reflections measured	9045	14,247
Number of unique reflections	2459	3666
Number of observed reflections $I > 2\sigma(I)$	2431	2862
Number of refined parameters	152	298
Goodness of fit on $F^2$	1.067	1.174
$R[F^2 > 2\sigma(F^2)], \ \mathrm{w}R_{2_{\mathrm{o}}}$	0.021, 0.056	0.045, 0.153
Residual density $(e \text{ Å}^{-3})$	-0.16, 0.25	-0.34, 0.28

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

1		2	
Co(1)–Cl(1)	2.2403(6)	Zn(1)– $Cl(1)$	2.2243(14)
Co(1) - N(1)	2.0313(13)	Zn(1)-Cl(2)	2.2360(14)
N(1) - C(12)	1.4037(19)	Zn(1)-N(1)	2.027(4)
N(1) - C(13)	1.307(3)	Zn(1)-N(3)	2.022(3)
N(2)-C(1)	1.428(3)	N(1) - C(1)	1.403(6)
N(2)–C(7)	1.391(2)	N(1)-C(13)	1.307(6)
N(2) - C(13)	1.352(2)	N(3) - C(14)	1.399(6)
C(7)-C(12)	1.388(3)	N(3)-C(26)	1.311(6)
Cl(1)-Co(1)-N(1)	109.12(4)	Cl(1)-Zn(1)-Cl(2)	121.20(6)
Cl(1)-Co(1)-Cl(1)a	116.53(2)	Cl(1)-Zn(1)-N(1)	102.43(12)
Cl(1)-Co(1)-N(1)a	109.34(5)	Cl(1)-Zn(1)-N(3)	112.36(12)
Cl(1)a-Co(1)-N(1)	109.34(5)	Cl(2)-Zn(1)-N(1)	109.52(12)
N(1)-Co(1)-N(1)a	102.46(5)	Cl(2)-Zn(1)-N(3)	102.13(11)
Cl(1)a-Co(1)-N(1)a	109.12(4)	N(1)-Zn(1)-N(3)	108.97(15)
Co(1) - N(1) - C(12)	132.33(12)	Zn(1) - N(1) - C(1)	128.2(3)
Co1-N1-C13	122.39(11)	Zn(1)-N(1)-C(13)	125.4(3)

Symmetry code: (a) 1 - x, y, 1 - z.

### 3. Results and discussion

1-Phenylbenzimidazole was synthesized from *N*-phenyl-1,2-diaminobenzene and formic acid in 4N HCl according to Phillips' method [17, 18]. The cobalt(II), zinc(II), nickel(II), copper(II), and iron(II) coordination compounds of 1-phenylbenzimidazole

Compound	Electronic absorption bands <sup>a</sup> , $\lambda_{max}$ (nm)		
	Intraligand and charge transfer bands	d–d Bands	Magnetic moment, $\mu_{\rm eff}$ (B.M.)
1-Phenylbenzimidazole	295, 245	_	_
1 2	470, 294, 212 292, 232, 223	675	4.13 Diamagnetic
3	273, 252, 237	453	2.88
4 5	286, 244, 233 280, 224, 215	439	1.71 2.40

Table 3. Electronic absorption spectral bands and magnetic moments of 1-phenylbenzimidazole and their complexes 1–5.

<sup>a</sup>DMSO used as a solvent.

were obtained through reflux in DMF. The complexes were crystallized from an EtOH/DMF mixture. The IR spectra of 1–5 are closely related to that of free 1-phenylbenzimidazole.

IR spectra of complexes show that the strong  $\nu_{(C=N)}$  in free 1-phenylbenzimidazoles at 1500 cm<sup>-1</sup> shifts to 1481 cm<sup>-1</sup> for Co(II), Zn(II), Ni(II), and Cu(II) complexes and to 1480 cm<sup>-1</sup> for Fe(II) complex. The red shift indicates that the tertiary nitrogen is coordinated. Such coordination of benzimidazoles to metal has been reported in the literature [4, 6, 8, 22–25]. In the far-IR spectrum a few new bands with respect to the 1-phenylbenzimidazole are observed. Bands at 330 and 251 cm<sup>-1</sup> for 1 correspond to  $\nu$ (Co–Cl) and  $\nu$ (Co–N<sub>benzimidazole</sub>), respectively. These bands are also observed at 311 cm<sup>-1</sup>,  $\nu$ (Zn–Cl) and 265 cm<sup>-1</sup>,  $\nu$ (Zn–N<sub>benzimidazole</sub>) for **2**, 347 cm<sup>-1</sup>,  $\nu$ (Ni–Cl) and 226 cm<sup>-1</sup>,  $\nu$ (Ni–N<sub>benzimidazole</sub>) for **3**, 345 cm<sup>-1</sup>,  $\nu$ (Cu–Cl) and 243 cm<sup>-1</sup>,  $\nu$ (Cu–N<sub>benzimidazole</sub>) for **5**.

As expected, coordination to Zn(II) and Fe(II) shifts the <sup>1</sup>H NMR signals of the complexes downfield from those of the free ligand ( $\Delta \delta = 0.59$  and 0.49 ppm, respectively) for the proton on 2-position of imidazole ring. The aromatic protons in Zn(II) complex were not shifted significantly downfield ( $\Delta \delta \approx 0.07$  ppm). But in Co(II), Ni(II), and Cu(II) complexes, unexpected upfield shifts were observed for the proton on the 2-position of imidazole ring and aromatic protons about 0.03-0.35 and 0.12-0.33 ppm. Aromatic protons of Fe(II) also showed upfield shifts of 0.10 ppm. These results arise from paramagnetic properties of Co(II), Ni(II), Cu(II), and Fe(II) atoms; the proton NMR of Co(II), Ni(II), Cu(II), and Fe(II) were recorded as broad peaks in diluted solvents with more scans. Even with these conditions, we could not observe carbon signals for these paramagnetic complexes. Similar broad <sup>1</sup>H-NMR peaks were also reported for paramagnetic complexes in the literature [16, 22]. The carbon peak on 2-position of imidazole ring of the ligand was shifted downfield about 1.83 ppm after coordination to Zn(II), which is very low compared to similar complexes containing alkyl-substituted benzimidazole complexes [16]. This unexpected shift probably arises from  $\pi$ -electron pushing of the phenyl group to the imidazole ring through space.

UV-Vis spectra of 1-phenylbenzimidazole and its complexes (1, 2, 3, 4, and 5) were determined from 190 to 800 nm in DMSO (table 3). 1-Phenylbenzimidazole has absorption maxima at 245 and 295 nm, attributed to  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions, respectively. In the complexes, these peaks shift to shorter wavelengths by 1–22 and

8–33 nm, respectively. The d–d bands for the cobalt(II), nickel(II), and copper(II) complexes **1**, **3**, and **4** were observed as 675 nm ( $\varepsilon = 489 \pmod{L^{-1}}^{-1} \text{ cm}^{-1}$ ), 453 nm ( $\varepsilon = 724 \pmod{L^{-1}}^{-1} \text{ cm}^{-1}$ ), and 439 nm ( $\varepsilon = 771 \pmod{L^{-1}}^{-1} \text{ cm}^{-1}$ ), respectively. The benzimidazole complexes studied here show tetrahedral geometry.

Co(II), Ni(II), Cu(II), and Fe(II) complexes (1, 3, 4, and 5) are paramagnetic with magnetic susceptibilities of 4.13, 2.88, 1.77, and 2.40 B.M., respectively.

## 3.1. Description of the crystal structure

A half of **1** connects on its other half by a two-fold rotation axis (symmetry code: (a) 1 - x, y, 1 - z) which passes through the cobalt and along the *b*-direction. The Co<sup>II</sup> is four-coordinate with two chlorides and two benzimidazoles. The coordination geometry is distorted tetrahedral with the Cl–Co–Cl angle, 116.53(2)°, being significantly larger than the Cl–Co–N angles (average 109.23 (5)°) and the N–Co–N angle (102.46 (5)°).

In 1, the average values of Co–N and Co–Cl bond lengths (2.0313(13) and 2.2403(6) Å) are nearly equal to the corresponding lengths in similar compounds [15, 26, 27]. The benzimidazole ring system (N(1)/N(2)/C(7)–C(13)) is almost planar, with maximum deviations of -0.017(2) Å for C(7), -0.015(2) Å for C(12), and 0.010(2) Å for C(10). The dihedral angle between the benzimidazole and phenyl rings (C(1)–C(6)) is 47.77(8)° [28]

In the crystal structure of **1**, molecular packing is stabilized by van der Waals interactions. Molecular conformation of **1** is stabilized by intramolecular C(11)– $H(11) \cdots Cl(1)$  interaction ( $C(11) \cdots Cl(1) = 3.5482(19)$ Å, C(11)– $H(11) \cdots Cl(1) = 142^{\circ}$ ). The molecular packing of **1** is shown in figure 2(a).

The central zinc in **2** is four-coordinate with two chlorides and two benzimidazoles in distorted tetrahedral geometry,  $Cl(1)-Zn(1)-Cl(2) = 121.20(6)^{\circ}$  ((Cl-Zn-N)<sub>average</sub> = 106.61(12)° and N(1)-Zn(1)-N(3) = 108.97(15)°). The Zn-N and Zn-Cl bond lengths (2.0313(13) and 2.2403(6) Å) are similar to those in similar compounds [21-23, 28]. The two benzimidazole rings in **1** are almost planar, with puckering parameters Q(2) = 0.026(5) Å,  $\phi(2) = 269(11)^{\circ}$  for N(1)/N(2)/C(1)-C(6)/C(13) and Q(2) = 0.009(5) Å,  $\phi(2) = 249(33)^{\circ}$  for N(3)/N(4)/C(14)-C(19)/C(26). The dihedral angle between them is  $64.82(17)^{\circ}$ . The phenyl rings with benzimidazole rings attached to them make dihedral angles of  $54.5(2)^{\circ}$  for (C(7)-C(12))<sub>phenyl</sub> and  $49.1(2)^{\circ}$  for (C(20)-C(25))<sub>phenyl</sub>, while the phenyl rings form a dihedral angle of  $51.8(3)^{\circ}$  with each other.

In the crystal structure of **2**, molecular packing is stabilized by weak  $\pi$ – $\pi$  stacking interactions [Cg2 ··· Cg5<sup>i</sup> = 3.947(3) Å and Cg5 ··· Cg5<sup>i</sup> = 3.728(3) Å; symmetry code: (i) 1 - x, 1 - y, 2 - z, where Cg2 and Cg5 are centroids of the N(3)/N(4)/C(14)/C(19)/C(26) 1 H-imidazole ring and the C(14)–C(19) benzene ring, respectively] and van der Waals interactions. The molecular packing of **2** is shown in figure 2(b).

#### 4. Conclusion

We have synthesized Co(II), Zn(II), Ni(II), Cu(II), and Fe(II) complexes of 1-phenyl benzimidazole, the first example of 1-phenyl-substituted benzimidazole



Figure 2. (a) The packing of 1 in the unit cell viewed down the *b*-axis. All hydrogens have been omitted for clarity. (b) The packing of 2 in the unit cell viewed down the *b*-axis. All hydrogens have been omitted for clarity.

metal complexes. X-ray diffraction analysis of dichlorobis(1-phenylbenzimidazole-1 *H*-benzimidazole- $\kappa N^3$ )cobalt(II) and dichlorobis(1-phenylbenzimidazole-1 *H*-benzimidazole- $\kappa N^3$ )zinc(II) show that cobalt and zinc are coordinated tetrahedrally by two chlorides and two nitrogens from two benzimidazole rings.

#### Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication CCDC Nos. 805619 (1) and 805620 (2). These data can be obtained free of charge *via* http:// www.ccdc.cam.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 E-mail: deposit@ccdc.cam.ac.uk.

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