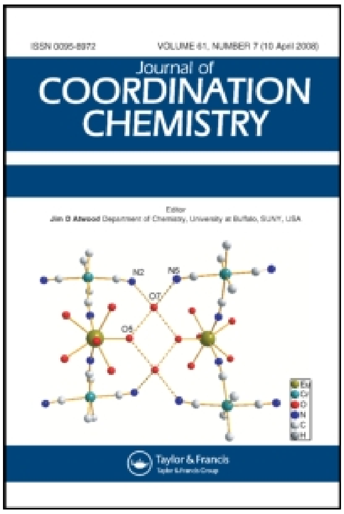


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structures and thermal properties of three crystalline polymorphs of the bis(*n*-phenylmethylbenzimidazole-*n*) dichloro cobalt(II) complex $CoCl_2(C_7H_5N_2CH_2Ph)_2$

Fangfang Jian[a]; Hailian Xiao[a]; Pingping Sun[a]; Udai Mukhopadhyay[b]; Ivan Bernal[b]
[a] New Materials and Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao, Shandong 266042, P.R. China [b] Chemistry Department, University of Houston, Houston, TX 77204-5003, USA

To cite this Article Jian, Fangfang , Xiao, Hailian , Sun, Pingping , Mukhopadhyay, Udai and Bernal, Ivan(2004) 'Synthesis, structures and thermal properties of three crystalline polymorphs of the bis(*n*-phenylmethylbenzimidazole-*n*) dichloro cobalt(II) complex $CoCl_2(C_7H_5N_2CH_2Ph)_2$', Journal of Coordination Chemistry, 57: 11, 923 — 934

To link to this Article: DOI: 10.1080/00958970410001726399

URL: http://dx.doi.org/10.1080/00958970410001726399

J. Coord. Chem., Vol. 57, No. 11, 20 July 2004, pp. 923–934

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, STRUCTURES AND THERMAL PROPERTIES OF THREE CRYSTALLINE POLYMORPHS OF THE BIS(*N*-PHENYLMETHYLBENZIMIDAZOLE-*N*) DICHLORO COBALT(II) COMPLEX $\mathrm{CoCl_2(C_7H_5N_2CH_2Ph)_2}$

FANGFANG JIAN[a],*, HAILIAN XIAO[a], PINGPING SUN[a],
UDAI MUKHOPADHYAY[b] and IVAN BERNAL[b]

[a]*New Materials and Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao, Shandong 266042, P.R. China;* [b]*Chemistry Department, University of Houston, Houston, TX 77204-5003, USA*

(Received 2 December 2003; Revised 1 March 2004; In final form 13 May 2004)

Three polymorphic, crystalline specimens of the bis(*N*-phenylmethylbenzimidazole-*N*)dichloro cobalt(II) complex $\mathrm{CoCl_2(C_7H_5N_2CH_2Ph)_2}$ have been obtained from different solvents and their structures determined by X-ray diffraction. X-ray analysis revealed that the three compounds have the same composition; however, details of their molecular structure differ significantly. The α-form is triclinic, space group $P\bar{1}$, with lattice parameters $a = 10.396(2)$, $b = 10.439(2)$, $c = 13.665(3)$ Å, $\alpha = 90.13(3)$, $\beta = 110.15(3)$, $\gamma = 110.46(3)^\circ$; both the β- and γ-forms crystallize in the monoclinic space group $P2_1/c$, with lattice parameters $a = 12.884(3)$, $b = 9.612(2)$, $c = 21.761(7)$ Å, $\beta = 108.02(3)^\circ$ for the β-form and $a = 7.357(2)$, $b = 18.337(4)$, $c = 19.572(5)$ Å, $\beta = 107.46(3)^\circ$ for the γ-form. In all three cases, the asymmetric unit consists of $\mathrm{[CoCl_2(C_7H_5N_2CH_2Ph)_2]}$ molecules. The geometry of their $\mathrm{CoCl_2N_2}$ chromophore is a distorted tetrahedron. Thermogravimetric analysis (TGA) indicates that they have different thermal stabilities and give rise to different resting residues. The electronic and IR spectra were also investigated. Analysis of the extent to which the stereochemistry of the constituent molecules in polymorphs A, B and C differ was examined using the program MATCHIT. There are major differences in the atomic positions of chemically related atoms that are not related to space group differences. The differences are caused by significant torsional motions of the flexible groups that seem to be caused by changes in the solvent media from which the crystals were obtained. Thus, the solvent cage of the parent solutions seems to be, at least partially, responsible for the incidence of crystalline polymorphism.

Keywords: Polymorphism; *N*-phenylmethylbenzimidazole; Co(II) complex; FT-IR spectra; TG-DSC; Conformational analysis; Solvent cage effects

INTRODUCTION

Benzimidazole is an interesting heterocyclic ring because it is present in various naturally occurring drugs, such as omeprazole, astemizole and emedastine difumarate [1].

---

*Corresponding author. Tel.: 86 532 4023606. Fax: 86 532 4022989. E-mail: ffj2003@163169.net

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001726399

The efficacy of substituted benzimidazoles in the treatment of parasitic infections is well known [2–4]. Interest in exploring benzimidazole derivatives and their metal complexes has increased, as many of these materials serve as models that mimic both the structure and reactivity of metal ion sites in complex biological systems [5,6]. Zinc(II), being a d^{10} ion, provides few spectroscopic signatures for monitoring of structure; however, Zn(II) can be substituted with the d^7 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 [7]. This is a general characteristic because the coordination chemistry of cobalt(II) is very similar to that of zinc(II) and the two metal ions also share almost identical ionic radii. In this paper, we report the synthesis and crystal structures of the three polymorphic, crystalline forms of bis(*N*-phenylmethylbenzimidazole-*N*)dichloro cobalt(II) complex. Elemental analyses, electronic and IR spectra, TGA and DSC data have also been recorded. The stereochemical variations of the molecular constituents observed in the three polymorphic forms were compared using superposition diagrams (MATCHIT figures).

EXPERIMENTAL

Physical Measurements

Elemental analyses were performed with a Perkin-Elmer 1400C analyzer. Infrared spectra were recorded on a Nicolet 170SX spectrometer using pressed KBr plates in the 4000–400 cm^{-1} range. Electronic spectra were recorded with a UV–Vis–NIR spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using an SDT 2980, simultaneously, for samples of *ca.* 10 mg under a nitrogen atmosphere (150 mL/min) at a heating rate of 10°C/min.

Preparation of the Cobalt(II) Complex

All chemicals were of analytical reagent grade and used as received. *N*-phenylmethylbenzimidazole was obtained by reacting benzimidazole with chloromethylbenzene under reflux. To a warm solution of *N*-phenylmethylbenzimidazole (2.2 g, 10.0 mmol) in EtOH (50 mL) was added with stirring $CoCl_2 \cdot 6H_2O$ (1.2 g, 5.0 mmol) and the mixture was refluxed for 40 min. The resulting blue solution was filtered and the filtrate heated to evaporate it. A blue solid appeared that was separated by filtration. The α-form single crystals were obtained by slowly evaporating a solution in EtOH open to the air. When CH_3CN and CH_3COCH_3 were used as solvents instead of EtOH, we obtained the β-form and the γ-form, respectively. The C, H and N content was determined by elemental analysis. Anal. Calcd. for $C_{28}H_{24}Cl_2CoN_4$ (%): C, 48.16; H, 4.77; N, 9.11. Found: α-form C, 47.72; H, 5.05; N, 8.87; β-form C, 47.42; H, 5.37; N, 8.92; γ-form C, 47.55; H, 5.25; N, 8.90.

Crystallographic Data Collection and Solution of Structure

Information concerning crystallographic data and structure refinement of the three compounds is given in Table I. The diffraction data were collected on a four-cycle CAD4 diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å,

TABLE I Summary of crystallographic data for the three polymorphs

	α	β	γ
Empirical formula	$C_{28}H_{24}Cl_2CoN_4$	$C_{28}H_{24}Cl_2CoN_4$	$C_{28}H_{24}Cl_2CoN_4$
Formula weight	546.34	546.34	546.34
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)	$a = 10.396(2)$, $\alpha = 90.13(3)$ $b = 10.439(2)$, $\beta = 110.15(3)$ $c = 13.665(3)$, $\gamma = 110.46(3)$	$a = 12.884(3)$ $b = 9.612(2)$, $\beta = 108.02(3)$ $c = 21.761(7)$	$a = 7.357(2)$ $b = 18.337(4)$, $\beta = 107.46(3)$ $c = 19.572(5)$
Volume (Å^3)	1291.6(5)	2563(1)	2518.9(1)
Z, Calculated density (Mg/m^3)	2, 1.405	4, 1.416	4, 1.441
Abs. coeff. (mm^{-1})	0.895	0.902	0.918
$F(000)$	562	1124	1124
Crystal size (mm)	0.30 × 0.25 × 0.18	0.25 × 0.20 × 0.15	0.25 × 0.18 × 0.15
Limiting indices	$-13 \leq h \leq 11$, $0 \leq k \leq 13$, $-17 \leq l \leq 17$	$0 \leq h \leq 15$, $-11 \leq k \leq 0$, $-25 \leq l \leq 24$	$-9 \leq h \leq 9$, $-23 \leq k \leq 0$, $-22 \leq l \leq 24$
Reflections collected/unique	3082/3082 [$R_{int} = 0.0000$]	4718/4502 [$R_{int} = 0.0871$]	6742/4259 [$R_{int} = 0.0605$]
Goodness-of-fit	0.866	1.120	0.867
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0456$, $wR_2^{a} = 0.0778$	$R_1 = 0.0666$, $wR_2^{b} = 0.1516$	$R_1 = 0.0405$, $wR_2^{c} = 0.0546$
R indices (all data)	$R_1 = 0.1383$, $wR_2^{a} = 0.0938$	$R_1 = 0.1534$, $wR_2^{b} = 0.1831$	$R_1 = 0.1285$, $wR_2^{c} = 0.0655$
Largest diff. peak and hole (e Å^{-3})	0.213 and −0.314	0.727 and −0.622	0.300 and −0.254

[a] $w = 1/[\sigma^2(F^2) + (0.0370P)^2]$, where $P = (F^2 + 2F^2c)/3$.

[b] $w = 1/[\sigma^2(F^2) + (0.0609P)^2 + 5.8086P]$, where $P = (F^2 + 2F^2c)/3$.

[c] $w = 1/[\sigma^2(F^2) + (0.0177P)^2]$, where $P = (F^2 + 2F^2c)/3$.

$T = 293$ K) radiation. The technique used was ω-scans with θ limits $1.60 < \theta < 27.53°$ for the α-form, $1.66 < \theta < 24.97°$ for the β-form and $1.56 < \theta < 27.50°$ for the γ-form. Empirical absorption corrections were carried out using the SADABS program [8]. The structures were solved by direct methods and refined by least squares on F_{obs}^2 by using the SHELXTL [9] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. Molecular graphics were generated using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [10].

RESULTS AND DISCUSSION

Crystal Structure of the Three Polymorphs

The molecular structure of the γ-form is illustrated in Fig. 1. Figure 2 shows a perspective view of the crystal packing in the unit cells for the three polymorphs. Selected bond distances and angles are listed in Table II. Although the molecules in the three polymorphs have different stereochemistry, B and C share a common space group ($P2_1/c$), while polymorph A crystallizes in the triclinic system. In these three polymorphs, the unit cells consist of monomeric $[CoCl_2(C_7H_5N_2CH_2Ph)_2]$ units and the coordination sphere around each cobalt(II) ion has a distorted tetrahedral arrangement, as the data in Table II show. The least distorted is the β-form. In the β-form,

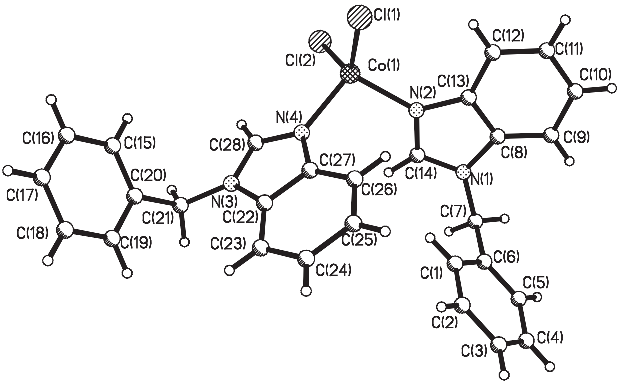
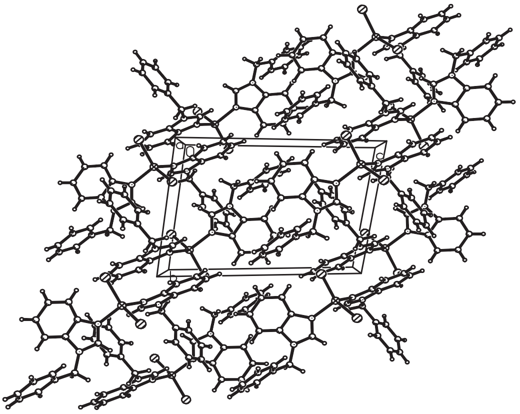


FIGURE 1 Molecular structure of the γ-form with the atom-numbering scheme.

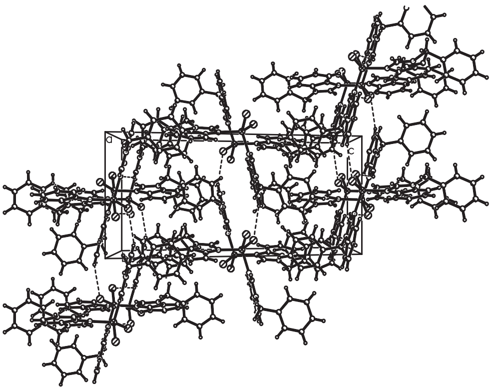
the highest value for the tetrahedral angles X–Co–Y is Cl(1)–Co–Cl(2) [115.71(8)°], which is about 6° greater than the ideal value. In the other two forms, the highest values are Cl(1)–Co–Cl(2) [119.44(8)°] for the α-form and Cl(2)–Co(1)–Cl(1) [117.47(4)°] for the γ-form. The Co–Cl bond lengths of 2.243(2) and 2.246(2) Å for the α-form, 2.237(2) and 2.252(2) Å for the β-form and 2.230(1) and 2.243(1) Å for the γ-form have an average value of 2.242(2) Å. These data are comparable with the corresponding values in the reported complexes Co(imidazole)$_2$Cl$_2$ [2.24(1) and 2.26(1) Å] [11] and Co(bdmpab)Cl$_2$ [2.243(8) and 2.227(8) Å; bdmpab = *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene] [12]. The Co–N bond lengths in the three isomers are nearly the same and comparable with the parameters obtained with the tetrahedral cobalt(II) complex Co(bdmpab)Cl$_2$ [2.038(2) and 2.044(2) Å] [12] but shorter than those of six-coordinate cobalt(II) complexes such as Co(cbim)$_4$(NO$_3$)$_2$ [2.109(2) and 2.134(3) Å; cbim = 4′-cyanobenzylimidazole] [13], [Co(imidazole)$_4$ (H$_2$O)$_2$] (C$_6$H$_4$COSO$_2$N)$_2$ [2.125(2) and 2.164(2) Å] [14] and [Co(imidazole)$_6$]$^{2+}$ [average 2.173 Å] [15] and longer than a square-planar cobalt(II) complex with CoN$_4$ core [average 1.875 Å] [16].

The benzimidazole ring [N(1), N(2), C(8)–C(14)] in the α-, β- and γ-forms, including the junction carbon atom [C(7)] and the metal atom [Co(1)], defines a fairly planar entity, whose largest deviation from the least-squares plane through the ring atoms is 0.064 Å for the α-form, 0.029 Å for the β-form and 0.011 Å for the γ-form. The second benzimidazole ring, including the junction carbon [C(14)] and the Co(1) atom, is also fairly planar, the largest deviation from the plane being 0.050 Å for the α-form, 0.016 Å for the β-form and 0.013 Å for the γ-form. The dihedral angles between the benzimidazole ring moieties and the attached phenyl rings are 88.98° and 89.49° for the α-form, 83.48° and 83.49° for the β-form, and 82.49° and 49.87° for the γ-form, respectively. The two benzimidazole moieties form a dihedral angle of 89.70° for the α-form, 72.53° for the β-form and 70.23° for the γ-form, while the dihedral angles between the phenyl rings are 80.71° for the α-form, 31.19° for the β-form and 22.75° for the γ-form, respectively.

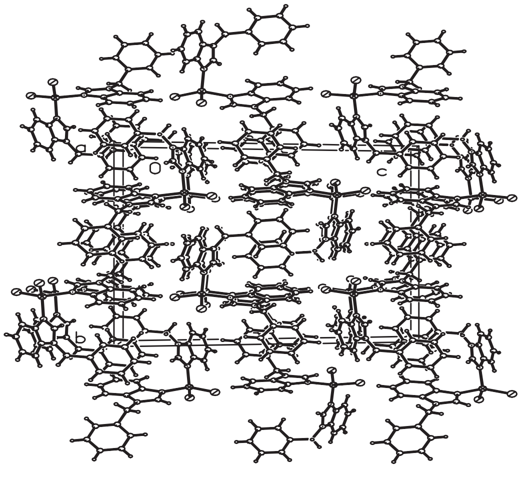
The molecules present in polymorphs A through C share some similarities. For example, they all have π–π stacking interactions [17,18] and C–H$\cdots\pi$ supramolecular interactions [19] between adjacent molecules in the crystal lattice. For the α-form,



α-form



β-form



γ-form

FIGURE 2 Packing diagrams of the unit cells of the three compounds.

TABLE II Selected bond lengths (Å) and angles (°) for the three polymorphs

	α	β	γ
Co(1)–N(4)	2.003(5)	2.007(5)	2.022(2)
Co(1)–N(2)	2.029(5)	1.997(5)	2.023(3)
Co(1)–Cl(1)	2.243(2)	2.237(2)	2.243(1)
Co(1)–Cl(2)	2.246(2)	2.252(2)	2.230(1)
N(4)–Co(1)–N(2)	103.9(2)	108.1(2)	103.07(1)
N(4)–Co(1)–Cl(1)	112.93(14)	110.62(15)	108.03(8)
N(2)–Co(1)–Cl(1)	109.37(16)	106.21(16)	110.45(9)
N(4)–Co(1)–Cl(2)	105.18(13)	107.45(15)	106.82(8)
N(2)–Co(1)–Cl(2)	104.62(15)	108.53(17)	109.94(8)
Cl(1)–Co(1)–Cl(2)	119.44(8)	115.71(8)	117.47(4)

there are three types of π–π stacking interactions: imidazole ring (X, Y, Z)–imidazole ring ($2-X$, $2-Y$, $-Z$), imidazole ring (X, Y, Z)–phenyl ring ($2-X$, $2-Y$, $-Z$) and phenyl ring (X, Y, Z)–imidazole ring ($2-X$, $2-Y$, $-Z$). The center-to-center distances are 3.707, 3.629 and 3.629 Å, respectively. The shortest interplanar distances above are 3.341 Å, 3.339 Å and 3.350 Å, respectively. There are six types of C–H$\cdots\pi$ supramolecular interactions between C–H and aromatic rings in the α-form. The distances between C(18)–H(18A) to the imidazole ring, C(2)–H(2A), C(3)–H(3A), C(7)–H(7B) and C(18)–H(18A) to the benzimidazole rings and C(21)–H(21A) to the phenyl ring are 2.878, 3.071, 3.068, 3.207, 2.889 and 3.157 Å, respectively. For the β-form and γ-form, there is one type of π–π stacking interaction: phenyl ring (X, Y, Z)–phenyl ring ($-1+X$, $3/2-Y$, $-1/2+Z$) for the β-form and phenyl ring (X, Y, Z)–phenyl ring ($3-X$, $1-Y$, $-Z$) for the γ-form, respectively. The center-to-center distance and the shortest interplanar distance are 3.995 and 3.283 Å for the β-form and 3.825 and 3.630 Å for the γ-form, respectively. There are four types of C–H$\cdots\pi$ supramolecular interactions in the β-form. The distances between C(15)–H(15A) and C(18)–H(18A) to the imidazole ring, C(16)–H(16A) to the benzimidazole rings and C(18)–H(18A) to the phenyl ring are 3.075, 2.769, 2.844 and 3.008 Å, respectively. There are five types of C–H$\cdots\pi$ supramolecular interactions in the γ-form. The distances between C(18)–H(18A), C(17)–H(17A) and C(4)–H(4A) to the imidazole ring and C(3)–H(3A) and C(16)–H(16A) to the phenyl ring are 3.054, 2.850, 2.893, 2.601 and 3.157 Å, respectively. In the solid state, all the above intermolecular interactions stabilize the crystal structures.

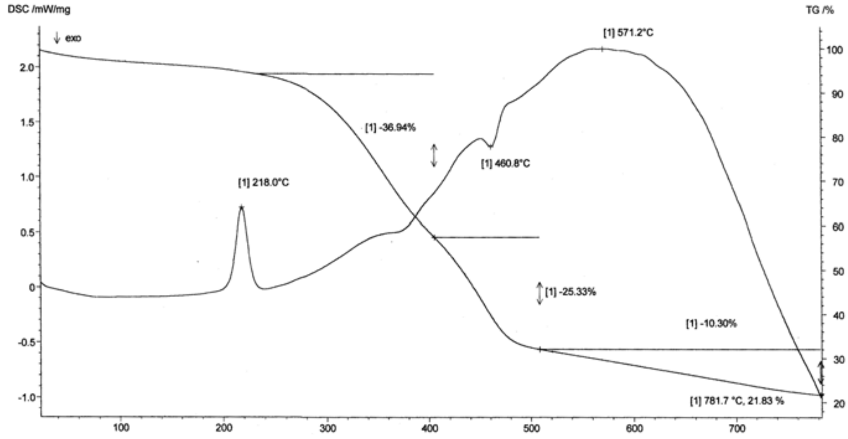
Spectral Characteristics

The IR spectra of the A, B and C forms show a slight difference. The two bands at 3429 and 2923 cm^{-1} for the α-form appear at 3104 and 2925 cm^{-1} for the β-form and at 3427 and 3105 cm^{-1} for the γ-form. These are assigned to the C–H stretching vibrations of the benzimidazole ring. All three polymorphs exhibit characteristically strong bands at about 1512 (C=C), 1461 (C=N), 753 ($\nu_{\text{C–H}}$ benzene ring) and 726 cm^{-1} ($\nu_{\text{C–H}}$ imidazole ring) for the coordinated benzimidazole ligands [20]. There is an obviously different ν(C=N) band at 1397 cm^{-1} for the α-form, 1388 cm^{-1} for the β-form and 1385 cm^{-1} for the γ-form. The bands at 1461 and 1397 cm^{-1} for the α-form, 1388 cm^{-1} for the β-form and 1462 and 1385 cm^{-1} for the γ-form are shifted from their positions in the free benzimidazole ligand (1454 and 1383 cm^{-1}) [21], indicating nitrogen coordination to the metal. The band at 494 cm^{-1} for these three stereoisomers is tentatively attributed to the ν(Co–N) bond.

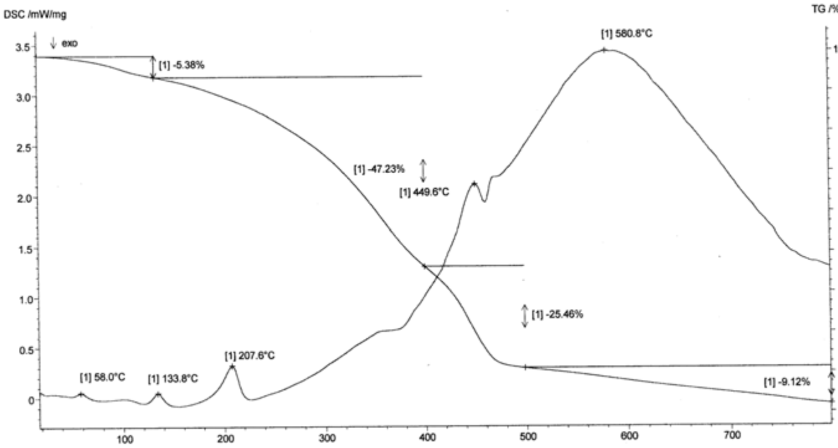
The solid reflectance electronic spectrum of the α-form shows two broad bands around 290 and 620 nm. The band around 290 nm is ascribed to intraligand interactions, probably a $\pi \rightarrow \pi^*$ transition of the benzimidazole group. The peak at 620 nm is a d–d transition of Co(II), which may be taken as evidence for tetrahedral Co(II) complexes [22]. The solid reflectance electronic spectrum of the β-form shows four broad bands around 215, 460, 485 and 510 nm. The band around 215 nm is ascribed to an intraligand transition of the benzimidazole group. The bands at 460, 485 and 510 nm are d–d electronic transitions of Co(II).

Thermal Analysis

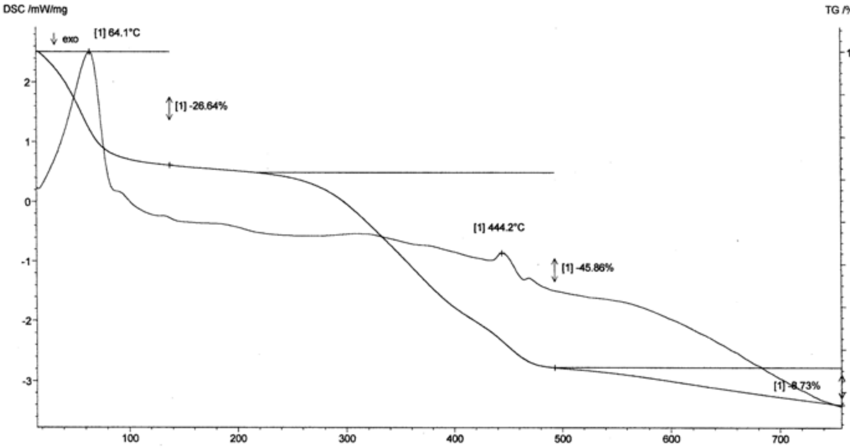
Thermal analysis curves of the title compound in the α-, β- and γ-forms are shown in Fig. 3. They are slightly different in their DTG curves. For the α-form, there are two endothermic peaks and one exothermic peak at 218.0, 571.2 and 460.8°C, respectively, indicating that the thermal decomposition process of the complex can be divided into three stages. In the first stage, between 198 and 240°C, no weight loss suggests that the compound melts. In the second stage, the complex is decomposed at 240–400°C, a weight loss of 36.94% is observed corresponding to the loss of a benzyl ring (found 36.94%, calc. 33.31%); then the decomposition continues, with an exothermic phenomenon at about 460.8°C. The weight loss of 25.33% suggests that a phenyl ring is lost (found 62.27%, calc. 61.13%). Finally, there is one broad endothermic peak at 571.2°C and a weight loss of 78.17% at 800°C suggesting that the residue should be $CoCl_2$ (found 78.17%, calc. 76.24%). For the β-form, four weight loss steps were noted. There is one weak endothermic peak in the DSC curve at 58.0°C, and about 5.38% weight loss in the TG curve between 58 and 133°C, which is attributed to the loss of a $-CH_2-$ group (found 5.38%, calc. 5.13%). The second weight loss may be related to the loss of a phenyl ring and decomposition of a benzimidazole ring, occurring at the two endothermic peaks at 133.8 and 207.6°C, respectively. Following the temperature increase, the Co–N bond cracks at the exothermic peak of 456.5°C. The weight loss of 78.07% suggests that the residue should be $CoCl_2$ (found 78.07%, calc. 76.24%). Finally, there is one intense broad endothermic peak at 580.8°C. Considering that the bond distance of Co(1)–Cl(2) [2.252 Å] is longer than other Co–Cl bond distances, we suggest that the Co(1)–Cl(2) bond was broken first, at the endothermic peak, then the Co(1)–Cl(1) bond was broken next. Because we selected the temperature range to be between 0 and 800°C, at 800°C the weight loss of 87.19% and the weight loss at the continuation of the curve suggest that the observed residue may be Co (found 12.81% at 800°C, calc. 10.78%). For the γ-form, there are three weight loss steps. One is a weak endothermic peak in the DSC curve at 64.1°C, and about 26.64% weight loss, which is attributed to the loss of a phenyl group (found 26.64%, calc. 27.82%). The second event may be related to loss of the $-CH_2-$ group and the benzimidazole ring, with one endothermic peak at 444.2°C (found 45.86%, calc. 45.39%). Following the temperature increase, disruption of the Co–Cl bonds takes place and the residue may be Co, as in the case of the β-form. From the thermal analysis above we can conclude that the α-form has better thermal stability than the β- and γ-forms.



α-form



β-form



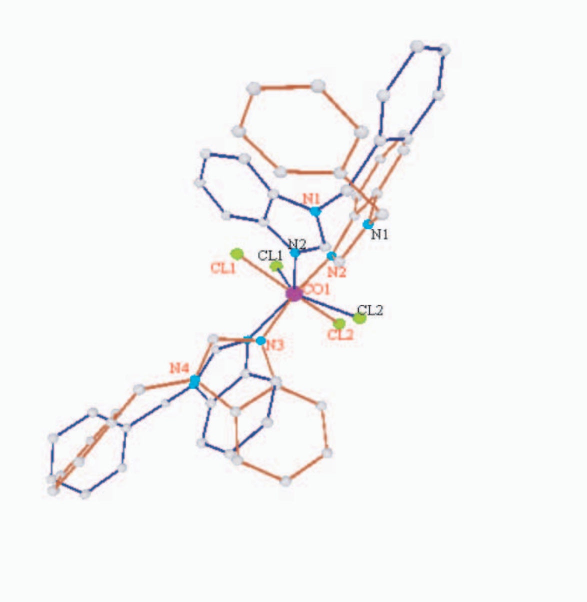
γ-form

FIGURE 3 TGA/DSC curves for the three compounds.

MATCHIT Examination of the Stereochemistry of the Molecules in the Three Polymorphs to Ascertain if Polymorphism is a Molecularly Driven Phenomenon

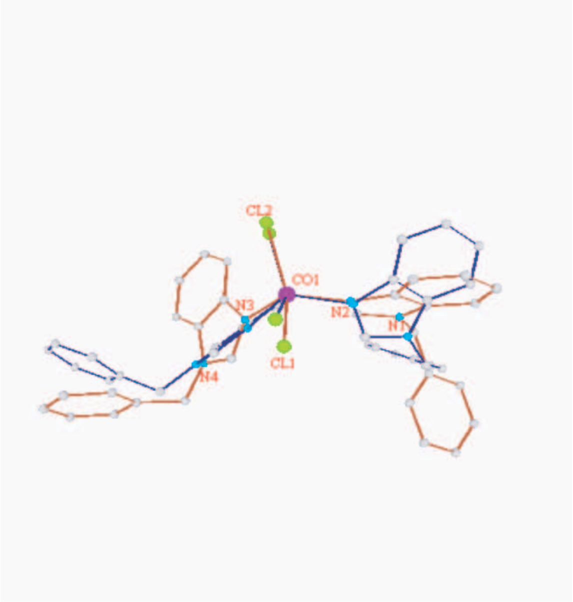
MATCHIT [23] was written to make graphical comparisons of molecules, or fragments of related chemical entities, together with tabular information of the distances between chemically related atoms. We have compared the geometrical characteristics of the molecules contained within the three polymorphic forms described in this study, as follows: Figs. 4–6 show a least-squares fitted attempt to superimpose B and C onto A, and C onto B.

In order to attain the best fit between B and C with A, and C with B, we had to define the atoms used in the least-squares fit. In all cases, the central metal, the two Cl and the two Ns defining the coordination sphere were selected. The other atoms were allowed to be guided into their positions by the results of the best fit.

Complex A vs B	Mean deviation of the atoms		
	Co1	Co1	0.000000
	Cl1	Cl1	1.460098
	Cl2	Cl2	1.535144
	N1	N1	1.304275
	N2	N2	0.992163
	N3	N3	1.031726
	N4	N4	2.610870
	C1	C1	2.591154
	C2	C2	1.920452
	C3	C3	0.695952
	C4	C4	2.031379
	C5	C5	2.938474
	C6	C6	2.853640
	C7	C7	4.186764
	C8	C8	1.595471
	C9	C9	1.561875
	C10	C10	1.463970
	C11	C11	1.908546
	C12	C12	1.525697
	C13	C13	0.928937
	C14	C14	2.237457
	C15	C15	2.878665
	C16	C16	4.368133
	C17	C17	4.975386
	C18	C18	4.684431
	C19	C19	3.246157
	C20	C20	1.595206
	C21	C21	0.944994
	C22	C22	2.727180
	C23	C23	4.195054
	C28	C28	0.522230
	C27	C27	2.564188
	C26	C26	3.934342

Red: Complex A
Blue: Complex B

FIGURE 4. A least-squares fitted attempt to superimpose β-form (blue) onto α-form (red).

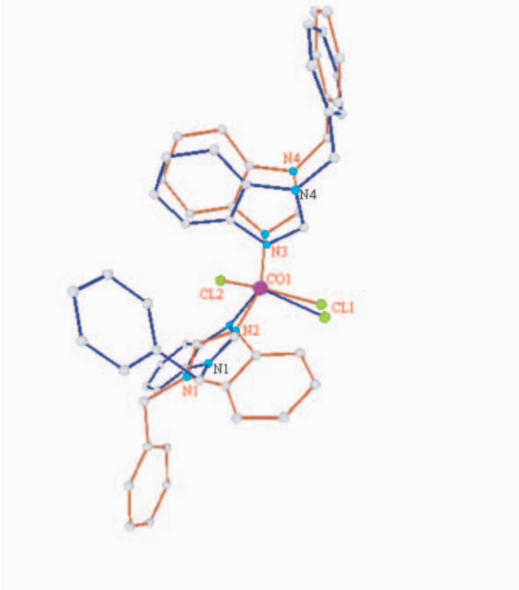
Complex Avs C	**Mean deviation of the atoms**		
	Co1	Co1	0.000000
	Cl1	Cl1	0.797808
	Cl2	Cl2	0.782455
	N1	N1	1.316531
	N2	N2	0.374090
	N3	N3	0.347538
	N4	N4	0.410514
	C1	C1	1.443866
	C2	C2	2.072759
	C3	C3	2.383376
	C4	C4	1.906978
	C5	C5	1.230595
	C6	C6	1.051371
	C7	C7	0.975724
	C8	C8	0.942855
	C9	C9	1.714142
	C10	C10	2.764587
	C11	C11	2.925315
	C12	C12	2.160337
	C13	C13	1.152255
	C14	C14	0.694386
	C15	C15	2.315256
	C16	C16	4.277160
	C17	C17	4.366872
	C18	C18	2.564107
	C19	C19	0.891986
	C20	C20	0.755190
	C21	C21	2.029998
	C22	C22	0.260027
	C23	C23	0.672524
	C24	C24	1.856465
	C25	C25	2.422618
	C26	C26	1.822760
	C27	C27	0.561504
	C28	C28	1.407808

Red: Complex A
Blue: Complex C

FIGURE 5. A least-squares fitted attempt to superimpose γ-form (blue) onto α-form (red).

The tables associated with Figs. 4–6 list all the distances between atoms of B and A, C and A, and B and C. Note that (a) some of the distances are quite large; for example, in Fig. 4, the pairs labeled C18 and C17 are separated, respectively, by 4.68 and 4.98 Å; and (b) C7 (CH2) pairs, about as far as possible given that they can only rotate torsionally, are 4.19 Å apart.

As is evident from the graphical results and from the tabular data, the three polymorphs differ markedly in their stereochemistry. For instance, Fig. 4 shows the best fit of B onto A. However, the fit is very poor, as exemplified by the fact that even the atoms used in the fit agree poorly. For example, related pairs of Cl ligands are separated by distances of *ca* 1.5 Å. The fit between C and A is somewhat better even though it is also not very impressive. Here the largest distances between related pairs occur at C11 (2.93 Å) and C17 (4.37 Å). Details are shown in Fig. 5 and in its table of distances.

Complex B vs C	**Mean deviation of the atoms**		
	Co1	Co1	0.000000
	Cl1	Cl1	1.383387
	Cl2	Cl2	1.481830
	N1	N1	1.846340
	N2	N2	1.240139
	N3	N3	0.501444
	N4	N4	1.262389
	C1	C1	1.376289
	C2	C2	2.267386
	C3	C3	3.704747
	C4	C4	4.434700
	C5	C5	3.587550
	C6	C6	1.976962
	C7	C7	2.082288
	C8	C8	0.941723
	C9	C9	1.237094
	C10	C10	1.734732
	C11	C11	1.975429
	C12	C12	1.463042
	C13	C13	0.816361
	C14	C14	1.100619
	C15	C15	4.998139
	C18	C18	3.967520
	C19	C19	1.879851
	C20	C20	2.465034
	C21	C21	1.984543
	C22	C22	3.312632
	C27	C27	3.090547
	C28	C28	1.129549
	C26	C26	4.793625

Red: Complex B
Blue Complex C

FIGURE 6. A least-squares fitted attempt to superimpose γ-form (blue) onto β-form (red).

At this juncture, we can ask if this poor fit may be attributed to the fact that A crystallizes in the triclinic system (space group $P\bar{1}$; No. 2) whereas B and C crystallize in the monoclinic system (both in space group $P2_1/c$). If this was the only factor causing the molecular rearrangements (and, thus, the polymorphism) the fit of B and C onto A should be more closely related in the distances between related atoms, which they are not. Moreover, the fit between C and B should be very much closer. Fig. 6 displays the graphical fit, as well as the table of interatomic distances, showing that C and B do not fit.

CONCLUSIONS

Three polymorphic forms of $CoCl_2(C_7H_5N_2CH_2Ph)_2$ were obtained by crystallizing the compound from different solvents. One crystallizes in the triclinic system, the other two in the monoclinic system sharing the same space group ($P2_1/c$). Even though B and C share the same space group, the best molecular fit between the molecules present in these polymorphs does not fit stereochemically significantly better than the fit between

A with B and C. This observation suggests that packing forces do not control the stereochemistry of these molecules in the solid state. Therefore, the nature of the solvent cages in the three solutions that the crystals came from must influence the topological features of the solute molecules and contribute to the observed stereochemical outcomes.

Acknowledgments

This work was supported by the Natural Science Foundation of Shandong Province (No. Y2002B06). U.M. and I.B. thank the Robert A. Welch Foundation for support of these studies (Grant 592 to IB) and for postdoctoral support to U.M.

Supplementary information

X-ray crystallographic files in CIF format have been deposited with the Cambridge Structural Database as files 211618, 211442 and 228493. The material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

References

[1] T. Sakai, T. Hamada, N. Awata and J. Watanabe, *Pharmacobio. Dyn.* **12**, 530 (1989).

[2] H.D. Brown, A.R. Matzuk, I.R. Ilves, L.H. Peterson, S.A. Harris, L.H. Sarett, J.R. Egerton, J.J. Yakstis, W.C. Campbell and A.C. Cuckler, *J. Am. Chem. Soc.* **83**, 1764 (1961).

[3] P.N. Preston, *Chem. Rev.* **74**, 279 (1974).

[4] B.R. Sarkar, B. Pathak, S. Dutta and S.C. Lahiri, *J. Indian Chem. Soc.* **61**, 151 (1984).

[5] E. Bouwman, W.L. Driessen and J. Reedijk, *Coord. Chem. Rev.* **104**, 143 (1990).

[6] M.A. Pujar, T.D. Bharamgoudar and D.N. Sathyanarayana, *Trans. Met. Chem.* **13**, 423 (1988).

[7] B.L. Vallee, J.F. Riordan, J.T. Johanson and D.M. Livingston, *Cold Spring Harbor Symp. Quant. Biol.* **36**, 517 (1971).

[8] G.M. Sheldrick, *Acta Cryst.* **A46**, 467 (1969).

[9] G.M. Sheldrick, *SHELXTL97: Program for Crystal Structure Refinement* (University of Göttingen, Germany, 1997).

[10] A.J. Wilson, *International Tables for X-ray Crystallography*, Vol. C (Kluwer, Dordrecht, 1992), Tables 6.1.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222).

[11] M. Laing and G. Carr, *Acta Cryst.* **B31**, 2683 (1975).

[12] H.L. Blonk, W.L. Driessen and J. Reedijk, *J. Chem. Soc., Dalton Trans.* 1699 (1985).

[13] W.Y. Sun, B.L. Fei, T. Okamura, Y.A. Zhang, T. Ye, W.X. Tang and N. Ueyama, *Bull. Chem. Soc. Jpn* **73**, 2733 (2000).

[14] J.M. Li, Y.G. Zhang, W.B. Lin, S.X. Liu and J.L. Huang, *Polyhedron* **11**, 419 (1992).

[15] Z.X. Wang, F.F. Jian, Y.R. Zhang, F.S. Li, H.K. Fun and K. Chinnakali, *J. Chem. Cryst.* **29**, 885 (1999).

[16] B.S. Jaynes, L.H. Doerrer, S. Liu and S.J. Lippard, *Inorg. Chem.* **34**, 5735 (1995).

[17] W. Xiao, Z.L. Lu, C.Y. Su, K.B. Yu, L.R. Deng, H.Q. Liu and B.S. Kang, *J. Mol. Struct.* **553**, 91 (2000).

[18] H. Masuda, T. Sugimori, A. Odani and O. Yamauchi, *Inorg. Chim. Acta* 73 (1991).

[19] R.H. Hunter, R.H. Haueisen and A. Irving, *Angew. Chem., Int. Ed. Engl.* **33**, 566 (1994).

[20] S.G. Wang, S.Y. Yu, Q.H. Luo, Q.Y. Wang, J.Q. Shi and Q.G. Wu, *Trans. Met. Chem.* **19**, 205 (1994).

[21] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn (Wiley, New York, 1970).

[22] H.B. Zhao, J. Cai, Y.B. Lin, Z.Q. Luo, J. Liu, J.H. Ning and J.H. Zhou, *Chin. J. Inorg. Chem.* **16**, 515 (2000).

[23] MATCHIT—a program for the superposition of molecules or fragments. The program can do a least-squares fit of chemically related atoms to improve the fit; it also calculates distances between common atoms. Written at the University of Houston by Rathnakumar Ramanujam under the guidance of Ivan Bernal.