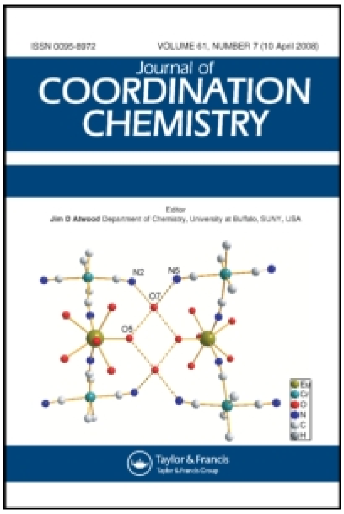

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Preparation and characterization of trimethylsilyl-substituted benzimidazole metal complexes and structural characterization of dichlorobis[1-(trimethylsilyl)methyl-1*H*-benzimidazole-κ*N*[3]]cobalt(II)

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Preparation and characterization of trimethylsilyl-substituted benzimidazole metal complexes and structural characterization of dichlorobis[1-(trimethylsilyl)methyl-1*H*-benzimidazole-κN^3]cobalt(II)

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The ligands 1-trimethylsilylmethylbenzimidazole, 5-methyl-1-trimethylsilylmethylbenzimidazole, and 5-nitro-1-trimethylsilylmethylbenzimidazole and their Co(II) and Zn(II) complexes were synthesized and characterized by ^{1}H-NMR, ^{13}C-NMR, and elemental analyses. The crystal structure of dichlorobis[1-(trimethylsilyl)methyl-1*H*-benzimidazole-κN^3]cobalt(II) has been determined by single crystal X-ray diffraction.

Keywords: Benzimidazole metal complexes; Silyl-substituted benzimidazoles; Crystal structure

1. Introduction

As components of biologically important molecules, imidazole and benzimidazole [1] have been the subject of numerous investigations [2–8]. Benzimidazole is a typical heterocyclic ligand with nitrogen donor and a component of biological important molecules [1, 4]. The benzimidazole ring is an important pharmacophore in modern drug discovery [9]. A large number of benzimidazole derivatives and their metal complexes are extensively investigated for versatile properties such as pharmacological [10–13] and catalytic activities of Pd [14, 15] and Ru [16] complexes. Antitumor properties of some silyl-substituted benzimidazoles and their metal complexes are also

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reported [17]. Transition-metal complexes of benzimidazoles are progressively being used to model important bio-inorganic systems [18].

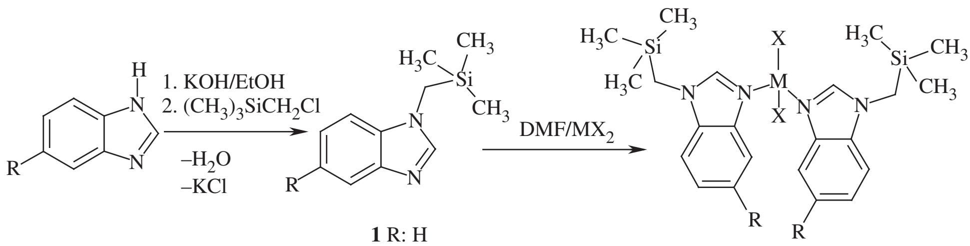
These results prompted us to synthesize silyl-substituted benzimidazoles and their metal complexes to investigate their structural, spectroscopic, and magnetic properties. We now report the preparation and characterization of three silyl-substituted benzimidazole derivatives and six corresponding metal complexes [Co(II), Zn(II)]. The crystal structure of dichloro-bis[1-(trimethylsilyl)methyl-1*H*-benzimidazole-κN^3] cobalt(II) was 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 were supplied commercially from Aldrich or Merck Chemical Co. Solvents were dried according to standard methods and freshly distilled prior to use. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded using a Bruker DPX-300 high-performance digital FT NMR spectrometer. Because of the paramagnetic properties of the cobalt atom, ^{1}H-NMR spectra of cobalt complexes were recorded as broad peaks through diluted sample solutions by increasing the scan number two times. Infrared spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} 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 were 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 and were corrected for diamagnetism by applying Pascal's constants. Compounds **1**–**3** were prepared by treating 5(6)-nitrobenzimidazole, 5(6)-methylbenzimidazole, and benzimidazole with (chloromethyl)trimethylsilane similar to the literature procedure [10]. Compounds **4**–**9** were synthesized from 1-(trimethylsilylmethyl)benzimidazoles with cobalt(II) and zinc(II) chlorides in DMF (scheme 1).

2.1. *Preparation of 1-(trimethylsilyl)methylbenzimidazole (1)*

(Chloromethyl)trimethylsilane (1.1 cm^3, 10 mmol) was added to a mixture of benzimidazole (1.18 g, 10 mmol) and KOH (0.56 g, 10 mmol) in EtOH (10 cm^3). The mixture was heated under reflux for 4 h, then cooled, and the precipitating potassium chloride was filtered off and washed with a little EtOH. The solvent was then removed from the filtrate *in vacuo*. The residue was washed with water (20 cm^3) two times and crystallized from EtOH/DMF (2 : 1). Yield: 1.592 g (78%); m.p.: 63–64°C. Anal. Calcd for $C_{11}H_{16}N_2Si$ (%): C, 64.65; H, 7.89; N, 13.71. Found (%): C, 64.63; H, 7.88; N, 13.65. IR: $\nu_{(C=N)}$: 1489 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): $\delta = 8.10$ (s, 1H, N=C*H*–N); 7.62 and 7.21 (m, 4H, Ar–*H*); 3.88 (s, 2H, CH_2Si); 0.03 ppm (s, 9H, Si(CH_3)$_3$). ^{13}C-NMR (DMSO-d$_6$): $\delta = 144.26$ (N=*C*H–N); 143.52, 134.92, 122.30, 121.46, 119.71, 111.01 (C_6H_4); 35.52 (N–*C*H_2–Si); −1.91 ppm (*C*H_3–Si).



1 R: H
2 R: CH_3
3 R: NO_2

4 R: H, M: Co, X: Cl
5 R: H, M: Zn, X: Cl
6 R: CH_3, M: Co, X: Cl
7 R: CH_3, M: Zn, X: Cl
8 R: NO_2, M: Co, X: Cl
9 R: NO_2, M: Zn, X: Cl

Scheme 1. Synthesis of the benzimidazoles and their metal complexes.

Similarly, compounds **2** and **3** were synthesized from (chloromethyl)trimethylsilane and 5(6)-methylbenzimidazole and 5(6)-nitrobenzimidazole, respectively.

2.2. *1-(Trimethylsilyl)methyl-5-methylbenzimidazole (2)*

Yield: 1.57 g, 72%; b.p.: 187–188°C. Anal. Calcd for $C_{12}H_{18}N_2Si$ (%): C, 66.00; H, 8.31; N, 12.83. Found (%): C, 65.96; H, 8.30; N, 12.79. IR: $\nu_{(C=N)}$: 1488 cm^{-1}. ^{1}H-NMR (DMSO-d_6): $\delta = 8.02$ (s, 1H, N=C*H*–N); 7.45 and 7.02 (m, 4H, Ar–*H*); 3.80 (s, 2H, CH_2Si); 2.40 (s, 3H, CH_3–Ar); 0.03 ppm (s, 9H, Si(CH_3)$_3$). ^{13}C-NMR (DMSO-d_6): $\delta = 144.09$ (N=*C*H–N); 141.96, 135.26, 130.81, 123.59, 119.32, 110.54 (C_6H_4); 35.35 (N–*C*H_2–Si); 21.69 (5-*C*H_3); −1.97 ppm (*C*H_3–Si).

2.3. *1-(Trimethylsilyl)methyl-5-nitrobenzimidazole (3)*

Yield: 2.02 g, 81%; m.p.: 161–162°C. Anal. Calcd for $C_{11}H_{15}N_3O_2Si$ (%): C, 52.99; H, 6.06; N, 16.85. Found (%): C, 52.91; H, 5.97; N, 16.74. IR: ν(C=N): 1490 cm^{-1}. ^{1}H-NMR (DMSO-d_6): $\delta = 8.54$ (s, 1H, N=C*H*–N); 8.17 and 7.85 (m, 3H, Ar–*H*); 4.02 (s, 2H, CH_2Si); 0.01 ppm (s, 9H, Si (CH_3)$_3$). ^{13}C-NMR (DMSO-d_6): $\delta = 148.58$ (N=*C*H–N); 142.86, 142.54, 139.20, 118.08, 116.12, 111.77 (C_6H_4); 36.25 (N–*C*H_2–Si); −2.06 ppm (*C*H_3–Si).

2.4. *Preparation of dichlorobis[1-(trimethylsilyl)methyl-1H-benzimidazole-κN^3] cobalt(II) (4)*

A solution of 1-(trimethylsilyl)methylbenzimidazole (2.0 g, 9.80 mmol) and cobalt(II) chloride (0.636 g, 4.90 mmol) in DMF (4 cm^3) was heated under reflux for 2 h. The mixture was then cooled to room temperature, after which the solvent was removed from the filtrate *in vacuo*. The obtained precipitate was then crystallized from

EtOH/DMF (2 : 1). Yield: 2.32 g (88%); m.p.: 126–127°C. Anal. Calcd for $C_{22}H_{32}N_4Si_2CoCl_2$ (%): C, 49.07; H, 5.99; N, 10.40. Found (%): C, 49.03; H, 5.91; N, 10.37. IR: $\nu_{(C=N)}$: 1482 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): 8.04 (s, 2H, N=C*H*–N); $\delta = 5.94$–6.33 (m, 8H, Ar–*H*); 3.99 (m, 4H, CH_2Si); 0.57 ppm (s, 18H, Si (CH_3)$_3$).

Similarly, compounds **5–9** were synthesized from 1-(trimethylsilyl)methylbenzimidazole or 1-(trimethylsilyl)methyl-5-methylbenzimidazole or 1-(trimethylsilyl)methyl-5-nitrobenzimidazole and $CoCl_2$ or $ZnCl_2$.

2.5. *Dichlorobis[1-(trimethylsilyl)methyl-1H-benzimidazole-κN^3]zinc(II) (5)*

Yield: 2.40 g, 90%; m.p.: 124–125°C. Anal. Calcd for $C_{22}H_{32}N_4Si_2ZnCl_2$ (%): C, 48.48; H, 5.92; N, 10.28. Found (%): C, 48.43; H, 5.91; N, 10.24. IR: $\nu_{(C=N)}$: 1483 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): $\delta = 8.48$ (s, 2H, N=C*H*–N); 7.79 and 7.30 (m, 8H, Ar–*H*); 4.05 (s, 4H, CH_2Si); 0.04 ppm (s, 18H, Si (CH_3)$_3$). ^{13}C-NMR (DMSO-d$_6$): $\delta = 162.75$ (N=*C*H–N); 144.65, 140.31, 134.15, 123.25, 118.57, 112.15 (C_6H$_4$); 36.25 (N–*C*H$_2$–Si); −2.08 ppm (*C*H$_3$–Si).

2.6. *Dichlorobis[1-(trimethylsilyl)methyl-5-methyl-1H-benzimidazole-κN^3] cobalt(II) (6)*

Yield: 2.23 g, 86%; m.p.: 140–141°C. Anal. Calcd for $C_{24}H_{36}N_4Si_2CoCl_2$ (%): C, 50.88; H, 6.40; N, 9.89. Found (%): C, 50.83; H, 6.37; N, 9.85. IR: $\nu_{(C=N)}$: 1486 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): $\delta = 7.95$ (s, 2H, N=C*H*–N); 5.60 and 6.40 (m, 6H, Ar–*H*); 3.95 (m, 4H, CH_2Si); 2.73 (s, 6H, CH_3–Ar); 0.36 ppm (s, 18H, Si (CH_3)$_3$).

2.7. *Dichlorobis[1-(trimethylsilyl)methyl-5-methyl-1H-benzimidazole-κN^3] zinc(II) (7)*

Yield: 2.34 g, 89%; m.p.: 131–132°C. Anal. Calcd for $C_{24}H_{36}N_4Si_2ZnCl_2$ (%): C, 50.30; H, 6.33; N, 9.78. Found (%): C, 50.24; H, 6.31; N, 9.74. IR: $\nu_{(C=N)}$: 1472 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): $\delta = 8.46$ (s, 4H, N=C*H*–N); 7.60 and 7.11 (m, 6H, Ar–*H*); 4.02 (s, 4H, CH_2Si); 2.34 (s, 6H, CH_3–Ar); 0.04 ppm (s, 18H, Si (CH_3)$_3$). ^{13}C-NMR (DMSO-d$_6$): $\delta = 162.75$ (N=*C*H–N); 144.23, 139.99, 132.90, 125.09, 117.81, 111.80 (C_6H$_4$); 36.24 (N–*C*H$_2$–Si); 21.61(5-*C*H$_3$); −2.12 ppm (*C*H$_3$–Si).

2.8. *Dichlorobis[1-(trimethylsilyl)methyl-5-nitro-1H-benzimidazole-κN^3] cobalt(II) (8)*

Yield: 2.30 g, 91%; m.p.: 200–201°C. Anal. Calcd for $C_{22}H_{30}N_6O_4Si_2CoCl_2$ (%): C, 42.04; H, 4.81; N, 13.37. Found (%): C, 42.01; H, 4.80; N, 13.35. IR: $\nu_{(C=N)}$: 1471 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): $\delta = 7.97$ (s, 2H, N=C*H*–N); 6.39 (m, 6H, Ar–*H*); 4.25 (m, 4H, CH_2Si); 0.21 ppm (s, 18H, Si (CH_3)$_3$).

2.9. *Dichlorobis[1-(trimethylsilyl)methyl-5-nitro-1H-benzimidazole-κN^3]zinc(II) (9)*

Yield: 2.40 g, 94%; m.p.: 189–190°C. Anal. Calcd for $C_{22}H_{30}N_6O_4Si_2ZnCl_2$ (%): C, 41.61; H, 4.81; N, 13.37. Found (%): C, 41.58; H, 4.79; N, 13.34. IR: $\nu_{(C=N)}$: 1472 cm^{-1}.

Table 1. Details of the data collection and refinement.

Crystal data	
$C_{22}H_{32}Cl_2CoN_4Si_2$	$Z = 4$
$M_r = 538.53$	$D_x = 1.227\,mg\,m^{-3}$
Monoclinic, $P2_1/c$	Mo-Kα radiation
$a = 13.6167(12)$ Å	Cell parameters from 6766 reflections
$b = 12.6780(12)$ Å	$\theta = 4.9$–$46.2°$
$c = 16.9081(14)$ Å	$\mu = 0.87\,mm^{-1}$
$\beta = 92.921(4)°$	$T = 293$ K
$V = 2915.1(4)$ Å^3	Plate, clear blue
Data collection	
APEX II QUAZAR diffractometer	$\theta_{max} = 25.0°$
ω and ϕ scans	$h = -16 \rightarrow 16$
Absorption correction: empirical (using intensity measurements)	$k = -15 \rightarrow 15$
$T_{min} = 0.910$, $T_{max} = 0.966$	$l = -20 \rightarrow 19$
25034 Measured reflections	
5133 Independent reflections	
3807 Reflections with $I > 2\sigma(I)$	
$R_{int} = 0.031$	
Refinement	
Refinement on F^2	H atoms constrained to parent site
$R[F^2 > 2\sigma(F^2)] = 0.037$	Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.3911P]$, where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.33$ e Å^{-1}
5133 Reflections	$\Delta\rho_{min} = -0.25$ e Å^{-1}
336 Parameters	Extinction correction: none

^{1}H-NMR (DMSO-d$_6$): $\delta = 8.62$ (s, 2H, N=C*H*–N); 8.15 and 7.89 (m, 6H, Ar–*H*); 4.07 (s, 4H, CH_2Si); 0.03 ppm (s, 18H, Si (CH_3)$_3$). ^{13}C-NMR (DMSO-d$_6$): $\delta = 162.77$ (N=*C*H–N); 148.66, 143.18, 134.08, 118.43, 115.84, 112.18 (C_6H_4); 36.30 (N–CH$_2$–Si); -2.11 ppm (CH$_3$–Si).

2.10. *Crystal structure determination of dichlorobis[1-(trimethylsilyl)methyl-1H-benzimidazole-κN^3]cobalt(II) and refinement details*

A clear blue plate-like crystal (0.04 mm × 0.06 mm × 0.11 mm) of [$C_{22}H_{32}Cl_2CoN_4Si_2$], **4** was measured on an APEX II QUAZAR. The X-ray data were collected at room temperature with a highly sensitive APEX II area detector using an IμS (microfocus source) with multilayer mirrors that give intense monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Details concerning crystal data and refinement are given in table 1. An empirical absorption correction was applied using SADABS 2008/1 [19]. The structure was solved by direct methods using SHELXS in the APEX2 Suite [20]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares technique using SHELXL [21].

Hydrogens were placed at calculated positions and treated as riding, with C–H = 0.93–0.97 Å, and U_{iso}(H) = 1.2 U_{eq}(C) for CH or 1.5 U_{eq}(C) for CH$_3$ atoms. Methyl groups bound to two silicons of the molecule are disordered over two positions with site occupancy factors of 0.42(4) and 0.58(4) for C9A/C9B, C10A/C10B, C11A/C11B, and 0.49(5) and 0.51(5) for C20A/C20B, C21A/C21B, and C22A/C22B. The Si–C bond lengths were restrained using SHELXL DFIX instructions for a standard Si–C bond value of 1.87 Å. A destructive phase transition has been detected even when cooling the crystal to 200 K. Therefore, the diffraction data has been collected at room temperature. It is not unusual that the $SiMe_3$ groups are not completely fixed and that the ADPs are enlarged in the rotation direction.

3. Results and discussions

1-(Trimethylsilyl)methyl-substituted benzimidazoles were synthesized from (chloromethyl)trimethylsilane and an appropriate benzimidazole by nucleophlic substitution reaction in high yields. The cobalt(II) and zinc(II) complexes of these benzimidazoles were obtained through reflux in DMF. The complexes were smoothly crystallized in an EtOH/DMF mixture. IR spectra of complexes show that the strong $\nu_{(C=N)}$ in free benzimidazoles at 1488–1490 cm^{-1} shifts to 1471–1486 cm^{-1} for Co(II) complexes and 1472–1483 cm^{-1} for Zn(II) complexes. The red shift indicates that the tertiary nitrogens of the ligands are coordinated to Co(II) and Zn(II), as reported for benzimidazoles to metals [3–7]. IR spectra of **3** showed absorption bands at 840, 1324, and 1512 cm^{-1} assigned to nitro attached to the 5-position of benzimidazole. Bands were observed at 848, 1330, and 1523 cm^{-1} for the corresponding Co(II) complex and 848, 1332, and 1524 cm^{-1} for the corresponding Zn(II) complex. The nitro group frequencies shifted slightly higher after coordination, perhaps from balancing the electron-withdrawing effect of nitro on free ligands after the formation of Co(II) and Zn(II) complexes. The carbon silicon band frequencies for starting 5H (**1**), 5-methyl (**2**) and 5-nitro benzimidazole (**3**) compounds were at 1239, 1416; 1230, 1416 and 1248, 1427 cm^{-1}, respectively. The carbon silicon band frequencies were observed between 1243–1247 cm^{-1} and 1410–1432 cm^{-1} for the metal complexes.

As expected, coordination to Zn(II) shifts the ^1H NMR signals of the complex downfield from those of the free ligand ($\Delta\delta \approx 0.08$–0.46 ppm) for the proton on 2 position of imidazole ring. The other peaks such as methylene and trimethyl protons attached to silicon and aromatic protons in Zn(II) complexes were not shifted significantly downfield ($\Delta\delta \approx 0.05$–0.17 ppm, 0.01–0.02 ppm, and 0.02–0.17 ppm, respectively). Comparing the free ligands, the peaks of methylene and trimethyl protons attached to silicon in Co(II) complexes were shifted downfield about 0.10–0.23 and 0.02–0.52 ppm, respectively. In Co(II) complexes, unexpected chemical shift to the upfield were observed for the proton on the 2-position of imidazole and aromatic protons about 0.06–0.57 and 1–1.5 ppm resulting from paramagnetic Co(II). As mentioned in Section 2, the proton NMR spectra were recorded as broad peaks in diluted solvents with more scans. Even in these conditions, we could not observe carbon signals. The carbon peak on 2-position of imidazole ring of the ligand shifted downfield about 14–18 ppm after coordination to Zn(II). Aromatic and methylene carbon peaks of the ligands were also shifted slightly downfield (about 1–4 ppm) after complexation with Zn(II). Both methyl protons and methyl carbons directly bonded to silicon in **1**–**3** were observed upfield as expected based on shielding. Because of the paramagnetic properties of the cobalt atom, we could not observe carbon peaks in the ^{13}C NMR spectra.

Table 2. Electronic absorption spectral bands and magnetic moments of **1**, **2**, **3** and their complexes **4–9**.

Compound	Electronic absorption bands,[a] λ_{max} (nm)		Magnetic moment, μ_{eff} (B.M.)
	Intraligand and charge transfer bands	d–d bands	
1	294, 209	–	–
2	295, 271, 258, 213	–	–
3	377, 259, 244	–	–
4	297, 264, 212	639	3.84
5	296, 247, 214	–	Diamagnetic
6	302, 236	635	3.92
7	298, 265, 246	–	Diamagnetic
8	389, 298, 259, 246, 213	675	3.98
9	401, 257, 207	–	Diamagnetic

[a]DMSO used as a solvent.

The UV-Vis spectra of free benzimidazoles (**1**, **2**, and **3**) and its complexes (**4–9**) were determined in 190–800 nm region in DMSO (table 2). Free substituted benzimidazoles have absorption maxima between 294–377 and 209–271 nm, attributed to π–π* and n–π* transitions, respectively. In the complexes, these peaks shift to longer wavelengths by 2–24 and 3–31 nm, respectively. The maximum bathochromic shifts were observed with substituted benzimidazole bearing NO_2 after coordination. The d–d bands for the cobalt(II) complexes **4**, **6**, and **8** were observed as 639 nm ($\epsilon = 55{,}372\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$), 635 nm ($\epsilon = 132{,}693\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$), and 675 nm ($\epsilon = 28{,}447\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$), respectively. Each of the cobalt(II) complexes shows a single d–d band. All Co(II) and Zn(II) benzimidazole complexes studied in this work show tetrahedral geometry. Since zinc(II) has no unpaired d-electrons, no absorption peak is observed in the visible region for these complexes. The cobalt(II) complexes (**4**, **6**, and **8**) are paramagnetic and their magnetic susceptibilities are 3.84, 3.92, and 3.98 B.M., respectively.

3.1. *Description of the crystal structure*

The cobalt in dichlorobis[1-(trimethylsilyl)methyl-1H-benzimidazole-κN^3]cobalt(II) (figure 1) is coordinated tetrahedrally by two chlorides and two nitrogens (table 1). The Cl_2N_2 donor set defines a distorted tetrahedron, with angles ranging from 104.23(7) to 115.62(4)° (table 3). The average Co–N bond length [2.007(2) Å] is almost equal to 2.008(2) Å in dichlorobis[1-(2-ethoxyethyl)-1*H*-benzimidazole-κN^3]cobalt(II) [22] and 2.032(2) Å in bis[1-(but-2-enyl)-5-nitro-1*H*-benzimidazole-κN^3]dichlorocobalt(II) [23]. This bond length may be compared with the corresponding values of 2.0944(14) Å in diaqua-bis(1*H*-imidazole-κN^3)bis(4-nitrobenzoato-κO)cobalt(II) [24] and 2.159(2) Å in diaqua-diformatodipyridinecobalt(II) [25]. The bond length is inversely related to the bond strength and bond-dissociation energy. Therefore, we can state that the Co–N bonds are strong.

The Co–Cl bond lengths of 2.2390(8) and 2.2208(10) Å in dichlorobis[1-(trimethylsilyl) methyl-1*H*-benzimidazole-κN^3]cobalt(II) are nearly equal to the corresponding bond lengths reported previously, namely 2.2525 (8) Å in quinolinium trichloro(quinoline-κN) cobaltate(II) [26] and 2.236 (1) Å in dichlorobis(1-propylimidazolidine-2-thione-κS) cobalt(II) [27] and 2.2680(8) Å in bis[1-(but-2-enyl)-5-nitro-1*H*-benzimidazole-κN^3]

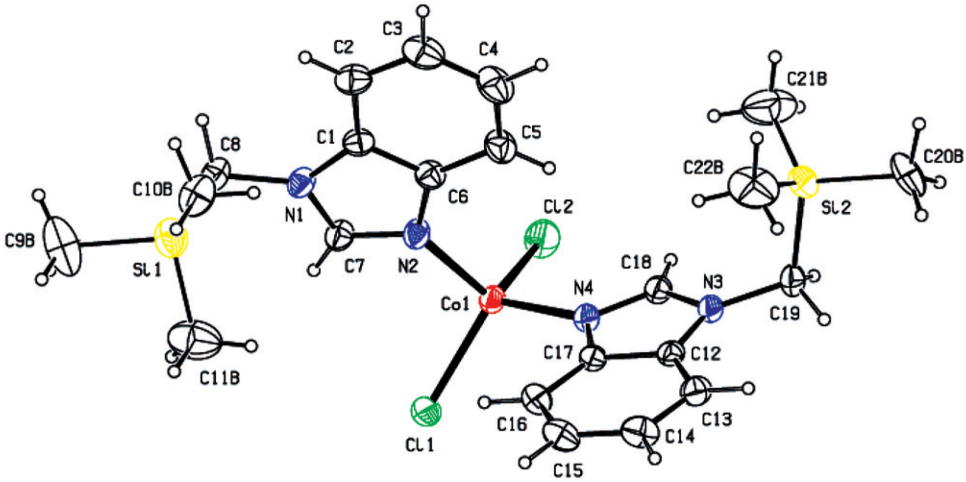


Figure 1. Molecular structure of dichlorobis[1-(trimethylsilyl)methyl-1*H*-benzimidazole-κN^3]cobalt(II) showing the atom-labeling scheme. The probability level for the anisotropic displacement parameters is 30%. Minor disordered sections are omitted for clarity.

Table 3. Geometric parameters (Å, °).

Co1–Cl1	2.2390(8)	Si1–C10A	1.84(4)
Co1–Cl2	2.2208(10)	Si1–C11A	1.90(3)
Co1–N2	2.000(2)	Si2–C19	1.890(3)
Co1–N4	2.014(2)	Si2–C20B	1.85(2)
Si1–C8	1.870(3)	Si2–C21B	1.86(3)
Si1–C9B	1.88(2)	Si2–C22B	1.858(16)
Si1–C10B	1.85(3)	Si2–C20A	1.87(3)
Si1–C11B	1.85(2)	Si2–C21A	1.85(2)
Si1–C9A	1.885(14)	Si2–C22A	1.868(12)
Cl1–Co1–Cl2	115.62(4)	C9A–Si1–C10A	111.8(15)
Cl1–Co1–N2	104.43(7)	C9A–Si1–C11A	132.6(15)
Cl1–Co1–N4	112.01(7)	C10A–Si1–C11A	98.4(19)
Cl2–Co1–N2	114.34(7)	C19–Si2–C20B	105.1(9)
Cl2–Co1–N4	104.23(7)	C19–Si2–C21B	109.6(9)
N2–Co1–N4	106.01(9)	C19–Si2–C22B	110.9(8)
C8–Si1–C9B	112.8(7)	C19–Si2–C20A	110.2(11)
C8–Si1–C10B	108.6(8)	C19–Si2–C21A	107.0(8)
C8–Si1–C11B	110.4(8)	C19–Si2–C22A	108.0(6)
C8–Si1–C9A	98.8(7)	C20B–Si2–C21B	113.7(12)
C8–Si1–C10A	111.5(14)	C20B–Si2–C22B	104.2(11)
C8–Si1–C11A	103.1(11)	C21B–Si2–C22B	112.9(12)
C9B–Si1–C10B	111.7(11)	C20A–Si2–C21A	107.6(13)
C9B–Si1–C11B	94.6(16)	C20A–Si2–C22A	119.8(13)
C10B–Si1–C11B	118.2(14)	C21A–Si2–C22A	103.4(10)
Cl1–Co1–N2–C6	152.7(2)	Cl1–Co1–N4–C18	132.6(2)
Cl2–Co1–N2–C6	−80.0(2)	Cl2–Co1–N4–C18	6.9(2)
N4–Co1–N2–C6	34.2(3)	N2–Co1–N4–C18	−114.1(2)
Cl1–Co1–N2–C7	−32.4(2)	C11B–Si1–C8–N1	−58.9(13)
Cl2–Co1–N2–C7	94.9(2)	C9B–Si1–C8–N1	−163.4(10)
N4–Co1–N2–C7	−150.9(2)	C10B–Si1–C8–N1	72.2(9)
Cl1–Co1–N4–C17	−49.4(2)	C22B–Si2–C19–N3	51.0(9)
Cl2–Co1–N4–C17	−175.1(2)	C20B–Si2–C19–N3	163.1(8)
N2–Co1–N4–C17	63.9(2)	C21B–Si2–C19–N3	−74.4(9)

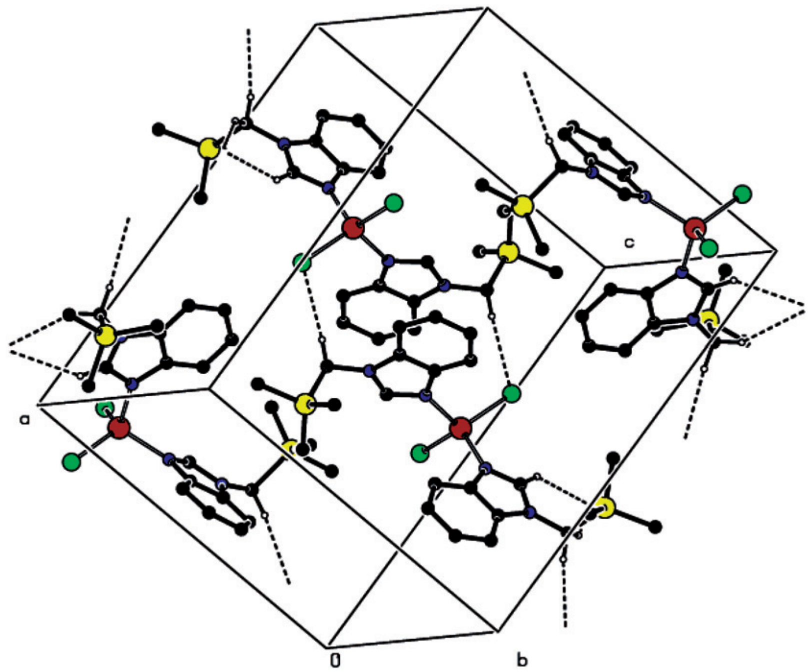


Figure 2. Packing view of dichlorobis[1-(trimethylsilyl)methyl-1*H*-benzimidazole-κN^3]cobalt(II) in the unit cell. Hydrogen bonds are indicated as dashed lines. Minor disorder and hydrogens not involved in hydrogen bonding have been omitted for clarity.

dichlorocobalt(II) [23]. However, they are shorter than the Co–Cl bond lengths observed in aquachlorobis(1,10-phenanthroline)cobalt(II)chloride dimethyl formamide solvate (2.391(1) Å) [28] and dichloridobis[5-nitro-1-trimethylsilylmethyl-1*H*-benzimidazole-κN^3]cobalt(II)-*N*,*N*-dimethyl-formamide solvate (2.2455(9) Å) [29].

The dihedral angle between the least-squares planes through the two benzimidazole ring systems is 81.86(12)°. The silicons have a distorted tetrahedral geometry with angles ranging from 94.6(16)° to 132.6(15)°; similar angles about silicon vary from 105.46(15) to 113.60(17)° in dichloridobis[5-nitro-1-trimethylsilylmethyl-1*H*-benzimidazole-κN^3]-cobalt(II)-*N*,*N*-dimethyl-formamide solvate [21].

The crystal packing of **4** shows individual molecules which are loosely associated into pairs *via* C–H···Cl hydrogen-bonding interactions (figure 2 and table 4) and C10B–H2E···Cg1($2-x$, $1/2+y$, $1/2-z$) interactions [H2E···Cg1 = 2.81 Å, C10B···Cg1 = 3.53(3) Å, C10B–H10E···Cg1 = 132°], where Cg1 is a centroid of the five-membered ring N1/C1/C6/N2/C7.

4. Conclusion

We have synthesized trimethylsilyl-substituted benzimidazole ligands and their Co(II) and Zn(II) complexes. X-ray diffraction analysis of dichlorobis[1-(trimethylsilyl)

Table 4. Hydrogen-bond parameters (Å, °).

	D–H	H···*A*	D···A	*D*–H···*A*
C7–H7···Cl1^{i}	0.93	2.79	3.575 (3)	142
C8–H8A···Cl1^{i}	0.97	2.83	3.709 (3)	151
C8–H8B···Cl2^{ii}	0.97	2.77	3.724 (3)	169
C19–H19B···Cl1^{iii}	0.97	2.75	3.710 (3)	169

Symmetry codes: (i) $2-x, -y, -z$; (ii) $2-x, 1/2+y, 1/2-z$; (iii) $1-x, -y, -z$.

methyl-1*H*-benzimidazole-κN^3]cobalt(II) shows that cobalt in this complex is coordinated tetrahedrally by two chlorides and two nitrogens from two benzimidazole rings.

Supplementary material

CCDC 760458 contains the supplementary crystallographic data for [$C_{22}H_{32}Cl_2CoN_4Si_2$]. 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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