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Synthesis, Structure and Spectroscopic Properties of Bis(2,4-dichloro-phenol-methylene--1H-benzimidazole-N^3)-dichlorocobalt(II)

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The title compound, CoL_2Cl_2 [L = (2,4-dichloro-phenol-methylene-1H--benzimidazole)], has been synthesized and structurally characterized by elemental analysis, IR and X-ray. The coordination geometry of cobalt(II) may be represented by slightly distorted tetrahedron with the CoN_2Cl_2 chromophore. In the solid state, the title compound forms infinite one-dimensional chains in the [101] direction through hydrogen bonds and potentially weak intermolecular interactions. The IR data agree with the crystal structure. The thermal gravimetry (TG) data indicate that there are two decomposition steps. The final product of thermal decomposition is Co_2O_3. The magnetic properties of the title compound are also reported and discussed.

Key words: crystal structure, dichlorocobalt(II) complex, benzimidazole substituted

Benzimidazole has an interesting heterocyclic ring, because it is present in various naturally occurring drugs, such as omeprazole, astemizole and emedastine difumarate [1]. The efficacy of substituted benzimidazoles in the treatment of parasitic infections is well known [2–4]. Benzimidazole-substituted moieties are established pharmacophores in parasitic chemotherapy. Bis(2-benzimidazoles) and some substituted bis(benzimidazol-2-yl)alkanes have attracted much interest, because of their wide-ranging antiviral activity [5], and also because of the coordination chemistry of azoles, acting as ligands in transition metal compounds. Such compounds are increasingly being studied in the context of modelling biological systems [6,7]. Zinc(II) being a d^{10} ion provides few spectroscopic signatures for the monitoring of structure, however, it 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 as much catalytic activity as the native zinc enzymes [8]. 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 report the synthesis and crystal structure of the title compound. The room temperature magnetic measurements, IR, and TG have also been investigated.

EXPERIMENTAL

Materials and physical measurements: All chemicals were of analytical reagent grade and used directly without further purification. Elemental analyses were measured 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} ranges. Magnetic measurements on powder samples were performed between 75–300 K by a Faraday-type magnetometer. TG and DTA curves were recorded on a NETZSCH-Geratebau GmbH thermoanalyser in flow of N_2, between 20°C – 800°C, with a heating rate 10°C/min.

Preparation of cobalt(II) complex: The ligand 2,4-dichloro-phenol-methylene-1H-benzimidazole was obtained by literature method [9]. The $CoCl_2 \cdot 6H_2O$ was dissolved in H_2O, ligand 2,4-dichloro-phenol-methylene-1H-benzimidazole was dissolved in EtOH. Cobalt dichloride aqueous solution was then added with stirring and the resulting solution was refluxed for 4–5 h, and then cooled. The light blue solution obtained was filtered and left to evaporate. After one day, blue solids were separated and were recrystallized from EtOH/H_2O. Single crystals suitable for X-ray analysis were obtained by slow evaporation from an EtOH solution at room temperature. The C, H and N contents were determined by elemental analysis.

RESULTS AND DISCUSSION

X-ray crystal structure determination: A summary of the key crystallographic information is given in Table 1. The diffraction data were collected on a SMART CCD diffractometer with graphite- monochromator, Mo-Kα radiation (λ = 0.71073 Å, T = 293 K). The technique used was ω-scan with limits $1.44 < \theta < 24.96°$. Empirical absorption correction was carried out by using the SADABS [10] program.

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{56}H_{40}Cl_{12}Co_2N_8O_4$
Formula weight	1432.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.8838(3) Å α = 93.750(1)°
	b = 11.1410(3) Å β = 108.104(1)°
	c = 13.9919(4) Å γ = 106.910(1)°
Volume	1520.08(7) Å^3
Z, Calculated density	1, 1.565 Mg/m^3
Absorption coefficient	1.126 mm^{-1}
F(000)	722
Crystal size	0.30×0.14×0.10 mm
Theta range for data collection	1.55 to 28.30 deg.
Limiting indices	–14<=h<=9, –10<=k<=14, –18<=l<=18
Reflections collected/unique	10816/7125 [R(int) = 0.0786]
Completeness to theta = 28.30	94.3%
Absorption correction	Empirical
Max. and min. transmission	0.8958 and 0.7288

Table 1 (continuation)

Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7125/0/370
Goodness-of-fit on F^2	0.855
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0671, wR2 = 0.1655
R indices (all data)	R1 = 0.1434, wR2 = 0.1997
Largest diff. peak and hole	0.565 and –0.887 e. Å^{-3}

The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the SHELXTL [11] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional R(F) = 0.0671 and wR (F^2) = 0.1655 for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(F^2) + (0.0699P)^2 + 0.0000P]$, where $P = (F^2 + 2Fc^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [12]. The final position parameters of non-hydrogen atoms are given in Table 2.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2\times 10^3$).

	x	y	z	U(eq)
Co(1)	–2380(1)	–573(1)	–2921(1)	41(1)
Cl(1)	–3628(2)	–2613(1)	–3602(1)	54(1)
Cl(2)	–280(2)	122(2)	–3010(1)	67(1)
Cl(3)	–3001(2)	4558(2)	–6203(1)	74(1)
Cl(4)	1723(2)	5265(2)	–6919(1)	74(1)
Cl(5)	–2333(2)	–3392(2)	1839(1)	86(1)
Cl(6)	–4605(2)	–8358(2)	155(2)	90(1)
O(1)	–2465(4)	2463(4)	–5317(3)	51(1)
O(2)	–2583(5)	–2962(4)	–138(3)	73(1)
N(1)	–3481(4)	537(4)	–3542(3)	34(1)
N(2)	–4303(4)	1881(4)	–4458(3)	41(1)
N(3)	–2090(4)	–277(4)	–1422(3)	44(1)
N(4)	–1723(5)	–484(5)	199(4)	54(1)
C(1)	–4633(5)	600(5)	–3328(4)	39(1)
C(2)	–5329(6)	–38(6)	–2745(4)	49(2)
C(3)	–6445(7)	203(7)	–2687(5)	66(2)
C(4)	–6980(6)	1028(7)	–3294(5)	70(2)
C(5)	–6341(6)	1693(6)	–3906(5)	56(2)
C(6)	–5183(5)	1434(5)	–3927(4)	43(1)
C(7)	–3301(5)	1339(5)	–4188(4)	37(1)
C(8)	–2149(6)	1617(5)	–4595(4)	46(1)
C(9)	–1452(5)	3038(5)	–5691(4)	41(1)

Table 2 (continuation)

C(10)	–350(6)	2659(6)	–5660(5)	61(2)
C(11)	614(7)	3313(6)	–6063(5)	59(2)
C(12)	501(6)	4385(6)	–6442(4)	49(2)
C(13)	–627(6)	4773(6)	–6519(4)	53(2)
C(14)	–1591(6)	4104(6)	–6129(4)	47(1)
C(15)	–1535(6)	938(5)	–785(4)	47(1)
C(16)	–1288(7)	2128(6)	–1106(6)	70(2)
C(17)	–765(7)	3156(7)	–302(6)	76(2)
C(18)	–598(8)	3012(8)	675(6)	83(2)
C(19)	–836(7)	1849(7)	981(6)	73(2)
C(20)	–1346(6)	800(6)	205(4)	48(1)
C(21)	–2130(6)	–1097(6)	–745(4)	44(1)
C(22)	–2662(7)	–2495(6)	–1028(5)	57(2)
C(23)	–3062(6)	–4244(6)	–158(5)	52(2)
C(24)	–2984(6)	–4588(6)	805(4)	49(1)
C(25)	–3457(6)	–5833(6)	899(5)	56(2)
C(26)	–4016(6)	–6767(6)	10(5)	59(2)
C(27)	–4078(7)	–6444(7)	–913(5)	66(2)
C(28)	–3607(7)	–5177(7)	–1004(5)	65(2)

Fig. 1 shows a perspective view of the title compound with atomic numbering scheme. Selected bond distances and angles are listed in Table 3. The environment around the Co atom is a distorted tetrahedral formed by two Cl atoms and two tertiary N atoms of the 2,4-dichloro-phenol-methylene-1H-benzimidazole ligands. The cobalt atom is coordinated tetrahedrally by two Cl^- anions and two 2,4-dichloro -phenol-methylene-1H-benzimidazole ligands. The $CoCl_2N_2$ tetrahedron is slightly distorted with angles ranging from 104.9(1)° to 116.99(7)°. The Co–Cl distances of 2.235(2) and 2.243(2) Å are comparable with the corresponding values in the reported complex $Co(imidazole)_2Cl_2$ [2.24(1) and 2.26(1) Å] [14] and $Co(bdmpab)Cl_2$ [2.2434(8) and 2.2266(8) Å; bdmpab = N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene] [15]. The Co–N distances of 2.011(5) and 2.019(4) Å are shorter than those of truly six-coordinate cobalt(II) complex such as $Co(cbim)_4(NO_3)_2$ [2.109(2) and 2.134(3) Å; cbim = 4′-cyanobenzyl-1-imidazole] [16], $[Co(imidazole)_4(H_2O)_2](C_6H_4COSO_2N)_2$ [2.125(2) and 2.164(2) Å] [17] and $[Co(imidazole)_6]^{2+}$ [average 2.173 Å] [18] and little longer than that of square-planar cobalt(II) complex with CoN_4 core [average 1.875 Å] [19], which are comparable with the tetrahedral cobalt(II) complex, $Co(bdmpab)Cl_2$, [2.038(2) and 2.044(2) Å] [15].

Table 3. Selected bond lengths [Å] and angles [°].

Co(1)–N(3)	2.011(5)	Co(1)–N(1)	2.019(4)
Co(1)–Cl(2)	2.2353(16)	Co(1)–Cl(1)	2.2433(16)
Cl(3)–C(14)	1.726(6)	Cl(4)–C(12)	1.748(6)
Cl(5)–C(24)	1.713(6)	Cl(6)–C(26)	1.749(6)
O(1)–C(9)	1.375(6)	O(1)–C(8)	1.457(7)
N(3)–Co(1)–N(1)	105.35(17)	N(3)–Co(1)–Cl(2)	104.89(13)
N(1)–Co(1)–Cl(2)	110.78(12)	N(3)–Co(1)–Cl(1)	109.76(13)
N(1)–Co(1)–Cl(1)	108.42(12)	Cl(2)–Co(1)–Cl(1)	116.99(7)
C(9)–O(1)–C(8)	116.1(4)	C(23)–O(2)–C(22)	120.2(5)

The benzimidazole rings with the conjunction of carbon and oxygen atoms are fairly planar, the deviations from the least squares plane through the ring atoms are 0.047(4) and 0.044(7) Å for plane 1 [C(1)~C(8), O(1), N(1) and N(2)] and plane 2 [C(15)~C(22), O(2), N(3) and N(4)], respectively. Plane 1 equation is $1.525x + 6.283y + 7.937z = -3.006$ and plane 2 equation is $10.791x - 3.326y - 2.58z = -1.785$. The two phenyl rings with the conjunction of chlorine and oxygen atoms are also quite planar, the largest deviation from the least squares plane are 0.046(7) Å and 0.050(8) Å respectively. The dihedral angles between the benzimidazole ring moieties and the conjunction phenyl ring are 13.9(1) and 4.1(2)°, respectively. The dihedral angles between the two planes of benzimidazole ring moieties are 76.6(2)°.

There are some intermolecular hydrogen bonds and potentially weak (C–H···Y hydrogen bonds, Y = O, N and Cl) intermolecular interactions. The N(2) and N(4) atoms of the benzimidazole moieties are involved in N–H···Cl intermolecular hydrogen bonds with the coordinated Cl atom. The N···Cl distances are 3.265(5) Å. The crystal packing is stabilized by extensive hydrogen bonding, the donor and acceptor distances are C(4)···Cl(2) 3.593(8) Å [sym. code: –1 + x, y, z];

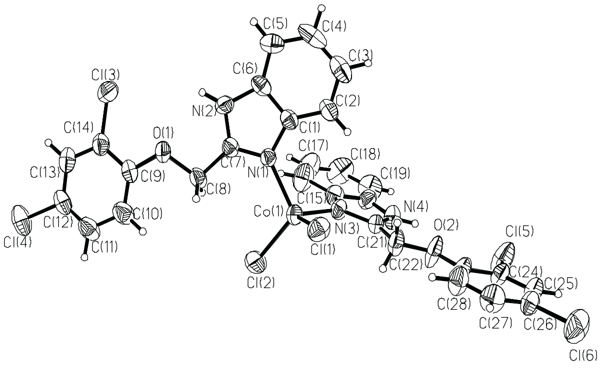

Figure 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

C(13)···Cl(5) 3.616(6) Å [sym. code: x, 1 + y, –1 + z]. These intermolecular hydrogen bonds link the molecules into infinite one-dimensional chains in the [101] direction.

"CCDC 206697 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* 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 336033; or deposit@ccdc.cam.ac.uk)".

Spectroscopic properties: In the IR spectra, there is a broad strong band in the 2500~3300 cm^{-1} region. It may be assigned to the C–H stretching vibration of the benzimidazole ring. The characteristic benzimidazole stretching vibration bands (C=C, C=N) in the 1623–1497 cm^{-1} region are shifted towards higher energy (*ca*. 10–23 cm^{-1}) [13] by coordinated to cobalt(II). The band at 540 cm^{-1} is tentatively attributed to ν(Co–N).

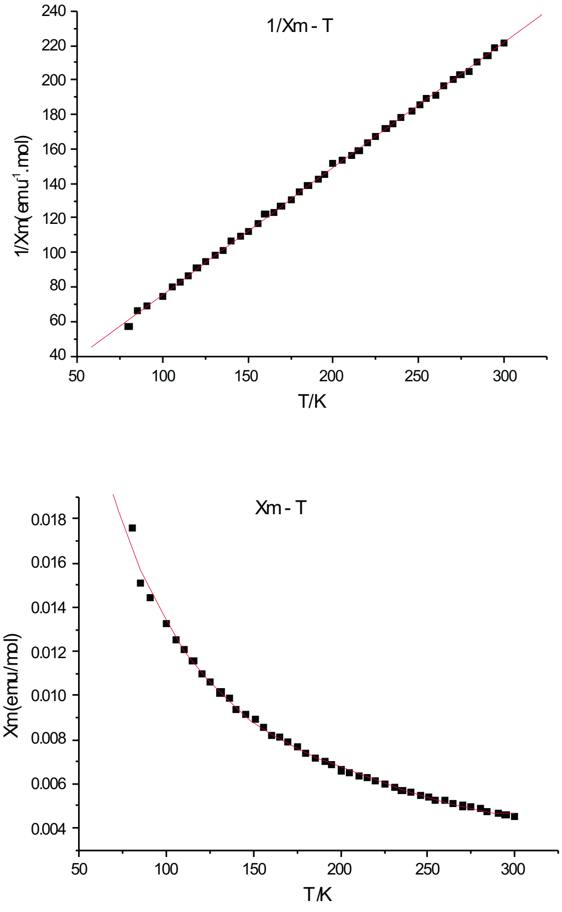

Figure 2. Experimental (■) and calculated (–) temperature dependent magnetic moment of the title compound.

The magnetic susceptibility as a function of temperature is shown in Fig. 2 in terms of $1/\chi_m$ *vs* T, where χ_m is the molar magnetic susceptibility per cobalt atom and T is the temperature. The complex obeys the Curie-Weiss law $1/\chi_m = C(T-\theta)$, with C = 0.627 $emu^{-1}\,K^{-1}$ mol and $\theta = -36.9$ K. This behaviour suggests that a very weak antiferromagnetic interaction operates between the cobalt(II) ions. The effective magnetic moment per cobalt atom at room temperature is 2.87 B.M., which is normal for the cobalt(II) ion in a tetrahedral environment.

Thermal results: The TG/DTC curves of the title compound are presented in Fig. 3. Thermogravimetric analysis (TGA) of the title compound reveals that the decompositions mainly take place at 277.1°C and 578.8℃, respectively. There are two heat-absorption peaks (284.5°C and 728.5℃). Decomposition begins at 277.1℃. On the basis of weight changes, the first change corresponds to the loss of methenyl benzimidazole in an endothermic process. The Co–N and O–CH_2 bonds decompose, the weight loss of 37.65% suggests that the residue should be $CoCl_2$(2,4-dichlorophenol)$_2$ (found 62.35%; calc. 62.35%). Then, above 323.6℃, $CoCl_2$(2,4-dichlorophenol)$_2$ begins to colapse. The two O-2,4-dichlorophenol moieties begin to dissociate. Finally, a 11.06% weight loss at 728.5℃ indicates the two chloro atoms loss with an endothermic peak. The residue may be Co_2O_3 (found 11.06%; calc. 11.59%).

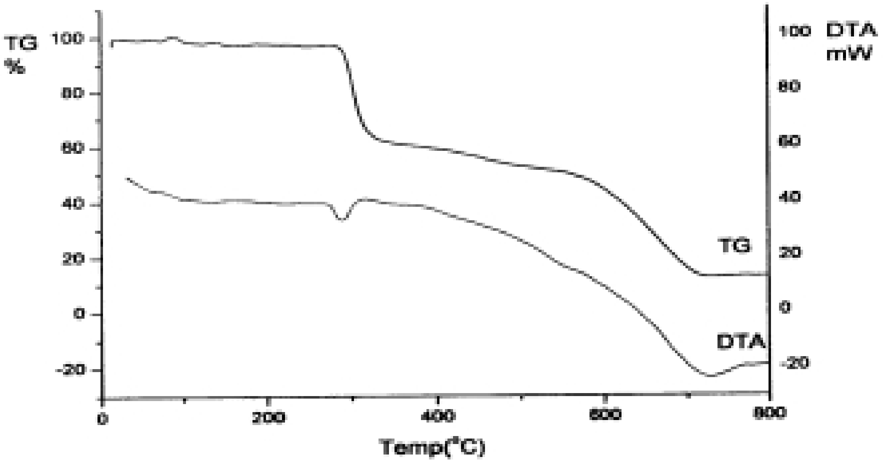

Figure 3. TG/DTC curves of the title compound.

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