

## КРАТКИЕ СООБЩЕНИЯ

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STRUCTURAL CHARACTERIZATION OF A NEW COBALT(II) COMPLEX OF  
1-BENZYL-5-METHYL-1H-IMIDAZOLE**M. Bouchouit<sup>1</sup>, A. Bouraiou<sup>1</sup>, S. Bouacida<sup>1,2</sup>, A. Belfaitah<sup>3</sup>, H. Merazig<sup>1</sup>**<sup>1</sup>*Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, Université des frères Mentouri, Constantine, 25000, Algérie*

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The preparation of a cobalt(II) chloride complex with a N-donor ligand 1-benzyl-5-methyl-1H-imidazole of formula  $[\text{CoCl}_2(1\text{-benzyl-5-methyl-1H-imidazole})_2]$  is described. The isolated complex was characterized by UV, IR spectroscopy and crystallographic studies. Single crystal X-ray diffraction analysis of the complex reveals its monomeric tetra-coordinated nature. The coordination polyhedron around the cobalt center can be described as a quasi-regular tetrahedron. The Co—N distances for this compound are 2.0111(17) Å and 2.0118(17) Å, while the Co—Cl distances are 2.2582(7) Å and 2.2549(7) Å. The crystal packing can be described as layers parallel to (101) plane alternating along the b axis, and it is stabilized by  $\pi$ — $\pi$  stacking between the imidazole and phenyl rings. The shortest centroid—centroid distance is 3.6002(14) Å.

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**Key words:** X-ray crystallographic analysis, imidazole, cobalt complex, crystal structure.

The use of small molecule model complexes to understand more complex biological systems has a long history [ 1, 2 ]. The imidazole nucleus is an important pharmacophore found in a large number of compounds with a wide range of applications, which make imidazole derivatives the subject of extensive investigations [ 3—5 ]. This entity is often employed as coordination ligand in the construction of diverse functional complexes not only because of its variable coordination modes, but also due to the inherent electronic effect [ 6, 7 ].

Complexes containing cobalt(II) ions are currently attracting considerable attention for their versatile properties and potential applications [ 8—10 ]. A significant interest has been attracted to the synthesis and characterization of cobalt(II) complexes in order to understand the properties of such species in a better way [ 11, 12 ].

Halide cobalt(II) complexes have also been extensively studied [ 13, 14 ], especially those containing chloro and bromo ligands. In this paper we report the synthesis and structural characterization of a mononuclear cobalt(II) complex derived from  $\text{CoCl}_2$  and 1-benzyl-5-methyl-1H-imidazole.

**Synthesis of 1-benzyl-5-methyl-1H-imidazole (L).** 10 mmol of 2-methyl-1H-imidazole was added to a suspension of potassium carbonate (10 mmol) in acetonitrile (10 mL), and then stirred for 15 min at r.t. 10 mmol of 1-(chloromethyl)benzene was added to the reaction mixture and the mixture was heated to 70 °C and kept for 72 h. After completion of the reaction, the solvent was removed and

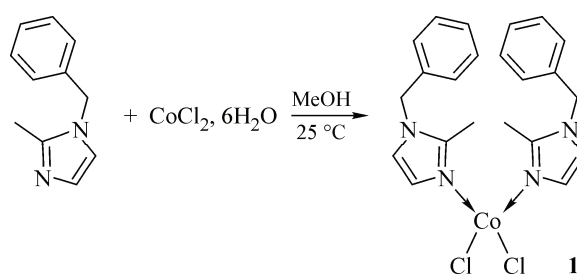
the residue was dissolved in EtOAc (20 mL), washed with H<sub>2</sub>O (2×10 mL) and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: CHCl<sub>3</sub>) to afford the desired product. Yield 38 %; yellow oil; UV-Vis (chloroform, λ, nm): 290; IR spectrum (KBr, ν, cm<sup>-1</sup>): 2939, 1712, 1508, 1434, 1365, 1272, 1118, 983, 721; <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>) δ: 7.43—7.32 (m, 5H), 7.17—7.14 (m, 2H), 6.99 (d, *J* = 1.3 Hz, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 5.11 (s, 2H), 2.27 (s, 3H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>) δ: 144.3, 138.0, 129.3, 128.1, 127.5, 127.1, 120.9, 49.2, 13.4.

**Preparation of [CoCl<sub>2</sub>L<sub>2</sub>] complex I.** A solution of 238 mg of CoCl<sub>2</sub>·6H<sub>2</sub>O (1 mmol) and 344 mg (2 mmol) of 1-benzyl-5-methyl-1*H*-imidazole (L) in 10 mL of MeOH was stirred overnight at room temperature. The blue precipitate of **1** formed was filtered off and dried *in vacuo*. Yield 85 %; m.p. 180 °C. UV-Vis (chloroform, λ, nm): 247, 580, 614, 633; IR spectrum (ATR): 3124, 2359, 1501, 1425, 1280, 1149, 1003, 727. Anal. calcd. for C<sub>22</sub>H<sub>24</sub>Cl<sub>2</sub>CoN<sub>4</sub>·0.1 CHCl<sub>3</sub>: C 54.59, H 5.00, N 11.52, found: C 54.23, H 4.98, N 11.53.

**Materials and methods.** All chemicals reagents and solvents were of analytical grade and were used as received. The melting point was determined using an Electrothermal IA9100 digital melting point apparatus. UV spectra were recorded on UV-Vis Spectrophotometer Optizen 1220; IR spectra were recorded on a JASCO FT/IR-6300 FT Infrared spectrometer and on a Shimadzu FT/IR-8201 PC spectrophotometer.

**X-ray crystallography.** The crystal of **1** was coated with Paratone oil and mounted on loops for data collection. X-ray data were collected with a Bruker Apex II CCD area detector diffractometer with a graphite-monochromated MoK<sub>α</sub> radiation source (0.71073 Å) at 298 K. The reported structure was solved by the direct methods with SIR2002 [ 15 ] to locate all the non-H atoms which were refined anisotropically with SHELXL97 [ 16 ] using full-matrix least-squares on *F*<sup>2</sup> procedure (WinGX [ 17 ] suite of software, also used to prepare material for publication). Absorption correction was performed with the SADABS program [ 18 ]. All H atoms were placed in the calculated positions and constrained to ride on their parent atoms. Crystal data and experimental parameters for compound **1** are listed in Table 1. Bond lengths and bond angles are listed in Table 2.

**Results and discussion. Synthesis.** The complex **1** was prepared as shown in Scheme 1. The ligand 1-benzyl-5-methyl-1*H*-imidazole (L) was stirred in MeOH with CoCl<sub>2</sub>·6H<sub>2</sub>O overnight at room temperature. The solid Co(II) complex was filtered off and dried. It is very stable in air and melts about 180 °C. The Co(II) complex is soluble in chloroform, DMF and DMSO but insoluble in water and other organic solvents, such as cold methanol. The crystals of complex **1** were obtained by slow evaporation of a chloroform solution at room temperature.



Scheme 1

**Crystal structure description.** Complex **1** crystallizes in the triclinic crystal system (space group *P*-1). The compound [CoCl<sub>2</sub>L<sub>2</sub>] (Fig. 1) is a tetracoordinated metal complex (Table 1). Cobalt(II) ion is surrounded by two N-donor atoms of the 1-benzyl-5-methyl-1*H*-imidazole ligand and by two chloride ligand. The complex contains two organic ligands of 1-benzyl-5-methyl-1*H*-imidazole further labeled as molecules a and b. Both molecules are characterized by two rings, N1a, C2a, N2a, C3a, C4a (Ring1 with centroid Cg1) and C6a, C7a, C8a, C9a, C10a, C11a (Ring 2 with centroid Cg2) and the same for molecule B, N1b, C2b, N2b, C3b, C4b (Ring 3 with centroid Cg3) and C6b, C7b, C8b, C9b, C10b, C11b (Ring 4 with centroid Cg4).

Cobalt(II) environment exhibits a quasi-regular tetrahedral coordination. The bond distances Co1—N1a and Co1—N1b are 2.0111(17) and 2.0118(17) Å, respectively, while the distance

Table 1

## Crystallographic data and refinement parameters for the complex I

Formula	C <sub>22</sub> H <sub>24</sub> Cl <sub>2</sub> CoN <sub>4</sub>
MW	474.28
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	7.0882(8), 11.9322(12), 14.1882(15)
$\alpha$ , $\beta$ , $\gamma$ , deg.	71.417(5), 86.927(4), 83.489(5)
<i>V</i> , Å <sup>3</sup>	1129.9(2)
<i>Z</i> ; <i>R</i> <sub>int</sub>	2; 0.038
Param. refined	264
<i>R</i> ( <i>F</i> <sup>2</sup> ) / <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.041 / 0.100
Crystal size, mm	0.03×0.04×0.12
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.394
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	1.011
<i>F</i> (000)	490
<i>hkl</i> range	-10 ≤ <i>h</i> ≤ 9, -16 ≤ <i>k</i> ≤ 16, -19 ≤ <i>l</i> ≤ 19
((sin $\theta$ )/ $\lambda$ ) <sub>max</sub> , Å <sup>-1</sup>	0.706
Reflections measured / unique	23311 / 6502
GOOF ( <i>F</i> <sup>2</sup> )	1.030
$\Delta\rho$ (max / min), e/Å <sup>3</sup>	0.51 / -0.31

Table 2

## Selected bond lengths (Å) and angles (deg.) for complex I

Bond lengths				Bond angles			
Co1—N1a	2.0111(17)	C2a—N1a	1.328(3)	N1a—Co1—N1b	114.29(7)	C2b—N1b—Co1	127.53(14)
Co1—N1b	2.0118(17)	C3a—N1a	1.379(3)	C11—Co1—N1b	105.97(5)	C3a—N1a—Co1	126.64(15)
Co1—C11	2.2582(7)	C2b—N1b	1.326(3)	N1a—Co1—C12	106.34(5)	C2a—N1a—C3a	105.81(17)
Co1—C12	2.2549(7)	C2b—N1b	1.382(3)	C11—Co1—C12	116.62(3)	C2b—N1b—C3b	106.27(18)

Co1—C11 is 2.2582(7) Å and the distance Co1—C12 is 2.2549(7) Å. Bond angles N1b—Co1—C11 and C11—Co1—C12 are 105.97(5)° and 116.62(3)°, respectively and the bond angle N1a—Co1—N1b is 114.29(7)°. The deviation of these values from the ideal value of 109° corresponding to the perfect tetrahedral geometry indicates some distortion.

The angles between rings 1 and 2 (molecule a) and 3 and 4 (molecule b) are 65.52(7)° and 66.63(1)° respectively, while the angle formed between the rings 2 and 4 is 27.14(1)°.

The crystal packing can be described as layers parallel to (101) plane alternating along the *b* axis (Fig. 2, *a*). In these layers, each molecule is

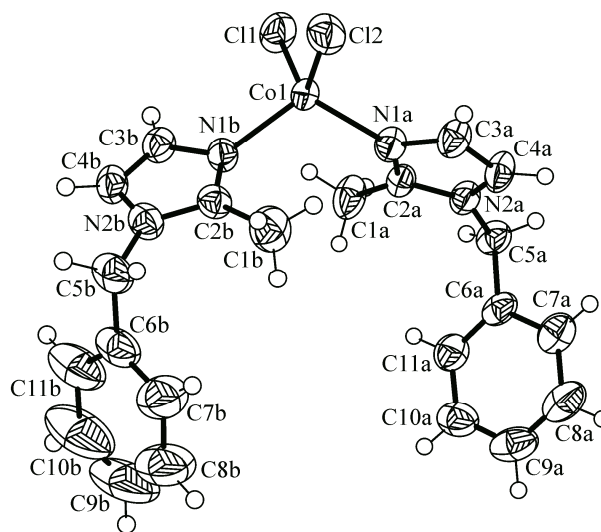


Fig. 1. Structure of complex I (thermal ellipsoids are shown with the probability of 50 %)

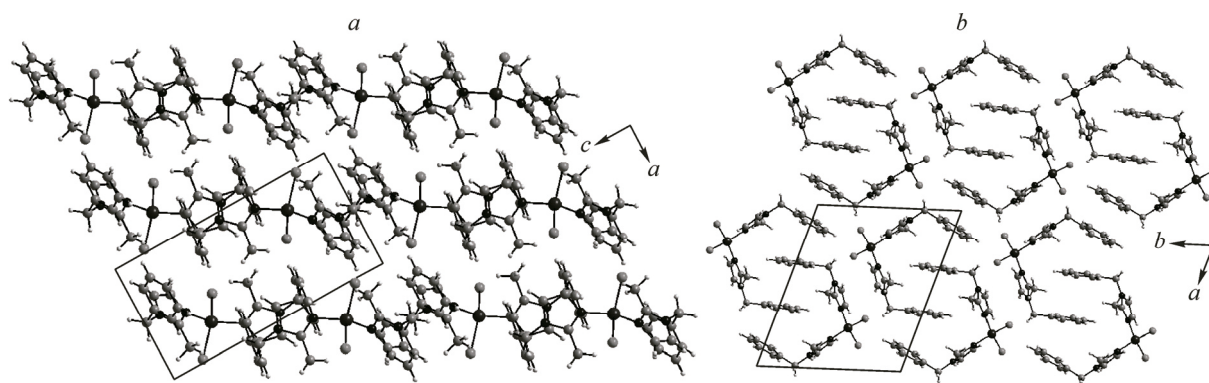


Fig. 2. View of the crystal structure of **I** in a projection along *b* axis showing alternating layers parallel to (101) plane (*a*), packing diagram of **I** viewed along the *c* axis (*b*)

*U*-shaped and overlaps with another one related by the inversion center (Fig. 2, *b*). This induces weak  $\pi$ — $\pi$  intermolecular interactions where the distances are 3.6002(14) Å for Cg1...Cg1, 3.6478(16) Å for Cg2...Cg2, 3.6444(15) Å for Cg3...Cg3 and 3.9350(2) Å for Cg4...Cg4. Also the complex presents a very weak intermolecular interaction C9b—H9b...Cg2i (*i* =  $-x$ ,  $-y$ ,  $-z+1$ ) where the distance of C...Cg is 3.732(5) Å and the C—H...Cg angle is 151°.

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with reference number 1409801. Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, UK (<http://www.ccdc.cam.ac.uk/>).

**Conclusions.** The synthesis and crystal structure of [CoCl<sub>2</sub>(1-benzyl-5-methyl-1*H*-imidazole)<sub>2</sub>] (**I**) has been described. In **I**, the cobalt atom has a quasi-regular tetrahedral geometry and the imidazole ring coordinates as a monodentate ligand.

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