

SYNTHESIS, X-RAY CRYSTAL STRUCTURE, SPECTROSCOPIC CHARACTERIZATION AND HIRSHFELD SURFACE ANALYSIS OF DICHLORO-BIS(3,5-DIMETHYL-4-AMINO-1H-PYRAZOLE) COBALT(II)

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The synthesis and characterization of mononuclear Co(II) complex based on 3,5-dimethyl-4-amino-1H-pyrazole are reported. IR and UV/Vis spectroscopy characterization of the complex are described. The synthesis, results of IR, NMR spectroscopy and elemental analysis of 3,5-dimethyl-4-amino-1H-pyrazole are also reported. X-ray analysis of $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$ complex reveals that the cobalt atom has a tetrahedral coordination environment formed by two nitrogen atoms belonging to the two 3,5-dimethyl-4-amino-1H-pyrazole ligands [$\text{Co1-N1} = 2.005(3)$ and $\text{Co1-N5} = 2.006(3)\text{\AA}$] and two chlorine atoms [$\text{Co1-Cl2} = 2.2400(11)$ and $\text{Co1-Cl1} = 2.2863(12)\text{\AA}$]. In the crystal structure the molecules are linked through intermolecular ($\text{N-H}\cdots\text{N}$, $\text{N-H}\cdots\text{Cl}$) and intramolecular non-classical ($\text{C-H}\cdots\text{Cl}$) hydrogen bonds. Hirshfeld surface analysis of the intermolecular contacts reveals that the most important contributions for the crystal packing are from $\text{H}\cdots\text{H}$ (47.1%) and $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ (28.5%) contacts.

Keywords: pyrazole, cobalt complexes, crystal structure, X-ray crystallography, Hirshfeld surface analysis.

INTRODUCTION. Pyrazole ligands are widely used in different areas of coordination, bioinorganic, supramolecular chemistry and in molecular electronics because of their marked tendency to form high nuclearity species exhibiting specific magnetic properties which also can be used for the development of structural and functional models of active sites of some metalloenzymes [1–2].

Transition metal complexes containing the pyrazole heterocycle are well studied [3–5].

Due to the presence of N-N bridging function in the pyrazole ring, these ligands can form polynuclear complexes with specific molecular topology. In this case, triangular azametallacrowns have been a much more common structure type [6–10]. The neutral pyrazole ligands usually bind to metal ions *via* the pyridine-type nitrogen atom and provide to form of the mononuclear complexes [11–14]. Despite the considerable amount of available data on the 3,5-substituted pyrazole compounds,

3,4,5-substituted pyrazole-based complexes have been studied very unevenly. We have been interested in how the steric factors, namely the presence of NH_2 substitute in the fourth position of the 3,5-dimethyl-1H-pyrazole, can influence the final crystal structure.

In this regard, in this work, we performed the synthesis of 3,5-dimethyl-4-amino-1H-pyrazole and Co(II) complex with it was also studied.

Although the X-ray structure of the title compound was previously reported [15], we used another solvent for the preparation of $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$. Additionally, IR and UV/Vis spectroscopic characterization of the complex are described. The synthesis, results of IR, NMR spectroscopy and elemental analysis of 3,5-dimethyl-4-amino-1H-pyrazole are also reported. Hirshfeld surface analysis of the intermolecular contacts of the title compound was also performed.

EXPERIMENT AND DISCUSSION OF THE RESULTS. All chemicals and solvents were commercial products of reagent grade and used without further purification. Microanalyses were performed with a Perkin – Elmer 2400 CHN. IR spectra (KBr pellets) were recorded with a Perkin – Elmer Spectrum BX FT-IR in the range of 400–4000 cm^{-1} . Absorbance UV/Vis spectra were registered with a Varian Cary 50 spectrophotometer in the range of 200–1000 nm at room temperature. ^1H NMR spectra were recorded on a Bruker AC-400 spectrometer (400 MHz) at room temperature. For X-ray structure determination, single crystals of $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$ were mounted on a Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated Mo K_α radiation source ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 293K. Effective absorption correction

was performed (SCALEPACK [16]). The structure of the complex was solved with the direct method using SIR-97 [17] software and was refined with full matrix least squares method on F2 using SHELXL-97 program [18]. H atoms were treated by a riding model. Crystallographic data are summarized in Table 1.

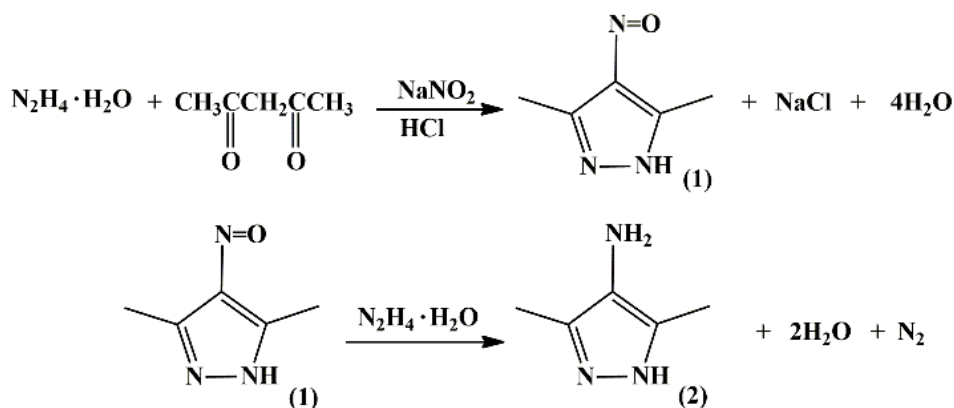
Table 1.

Crystal data and structure refinement for $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$.

<i>Chemical formula</i>	$\text{C}_{10}\text{H}_{18}\text{Cl}_2\text{CoN}_6$
<i>Mr</i>	352.13
<i>Crystal system, space group</i>	Triclinic, $P - 1$
<i>Temperature (K)</i>	293
<i>a (Å)</i>	9.2036(7)
<i>b (Å)</i>	9.2100(8)
<i>c (Å)</i>	10.0872(8)
α (°)	94.738(5)
β (°)	106.089(5)
γ (°)	107.844(5)
<i>V (Å³)</i>	768.81(11)
<i>Z</i>	2
<i>Density (Mg/m³)</i>	1.521
<i>Radiation type</i>	Mo K_α
μ (mm ⁻¹)	1.46
<i>Crystal size (mm)</i>	0.15 × 0.15 × 0.1
<i>F(000)</i>	362
<i>Theta range θ, (°)</i>	0.998–27.485
<i>Reflections collected</i>	3365
<i>G.O.F.</i>	1.007
<i>Final R indices</i> <i>R1 ma wR2 [$I > 2\sigma(I)$]</i>	$R1 = 0.0951$ $wR2 = 0.0471$
<i>R indices</i> <i>R1 ma wR2 (all data)</i>	$R1 = 0.1298$ $wR2 = 0.1075$
<i>Largest diff. peak and hole (e. Å⁻³)</i>	0.396, -0.561

The synthesis of 3,5-dimethyl-4-amino-1H-pyrazole (L) was carried out according to the following method. 50 g (0.50 mol) of freshly distilled acetylacetone, 45 mL of concentrated HCl and 250 mL of water were placed into a four-neck 1L round bottom flask equipped with a stirrer, reflux condenser, thermometer, and addition funnel. The mixture was cooled with stirring in an ice bath to 5 °C and a solution of NaNO₂ (36 g; 0.52 mol) in 100 mL of water was dropwise added to it over 10–15 minutes. After consecutive stirring for 20 min, 27.5 g (0.55 mol) of 85% hydrazine hydrate was added to the reaction mixture. After that 85 g of NaCl was added to the reaction flask to precipitate the product and the mixture was stirred for 1.5 hours at r.t. The obtained blue crystals were

filtered off and air-dried. Subsequent treatment of the isolated product by refluxing of its mixture with anhydrous benzene (800 mL) during 5–7 min allowed to selectively dissolve 3,5-dimethyl-4-nitroso-1H-pyrazole (1), in Scheme 1, whereas NaCl was insoluble in these conditions and was filtered off from the hot solution. Slow cooling of the filtrate to 10 °C led to the crystallization of 3,5-dimethyl-4-nitroso-1H-pyrazole (m.p. 128–129 °C), which turned green in the air. To increase the yield of the product, the filtered off (on the first purification step) solid was mixed with the filtrate and obtained mixture was refluxed, filtered and the new filtrate was cooled to 10 °C, which led to the second portion of the product. Yield: 62.5 g; 90%.



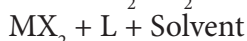
Scheme 1. Synthesis of 3,5-dimethyl-4-amino-1H-pyrazole.

Hydrazine hydrate (90%, 93 mL; 0.5 mol) was added to 3,5-dimethyl-4-nitroso-1H-pyrazole (62.5 g; 0.5 mol) in ethanol (650 mL) and placed into a three-neck round-bottom flask equipped with a stirrer, reflux condenser, and thermometer. At that temperature of reaction mixture increased to 60–65 °C. The mixture was refluxed under constant stirring for 3 hours, which was accompanied by its color change from green to

yellow-brown. The solvent was completely distilled off and the resulting crystalline residue was washed with cold ethanol (20–25 mL) and air-dried. The yield of the crystalline product (2), in Scheme 1, was 52.0 g (93%). ¹H NMR (DMSO-d₆), δ: 2.11 (s, 6H; 2CH₃), 6.10 (s, 2H; NH₂), 12.55 (br. s., 1H; NH). Elemental analysis: calculated (%): C 54.05; H 8.11; N 37.83. Found: C 54.04; H 8.10; N 37.85.

The preparation of the title compound was carried out according to the following method. Cobalt (II) chloride hexahydrate (0,0071 g, $3 \cdot 10^{-5}$ mol) and 3,5-dimethyl-4-amino-1H-pyrazole (0,0033 g, $3 \cdot 10^{-5}$ mol) were dissolved in methanol (1 mL). The blue mixture was stirred for 15 min at ambient temperature. The resulting blue solution was left to stand at room temperature. Slow evaporation of the solvent in 2 days yielded the blue crystals of the mononuclear complex (Scheme 2). Yield 93%. Elemental analysis: calculated (%): C 34.09; H 5.11; N 23.86. Found: C 34.03; H 5.10; N 23.85.

The synthesis of coordination compounds with 3,5-dimethyl-4-amino-1H-pyrazole (L) was performed with various salts (MX_2) of different 3d-metals, but crystals suitable for X-ray were obtained only in the case of interaction of L with $CoCl_2 \cdot 6H_2O$.

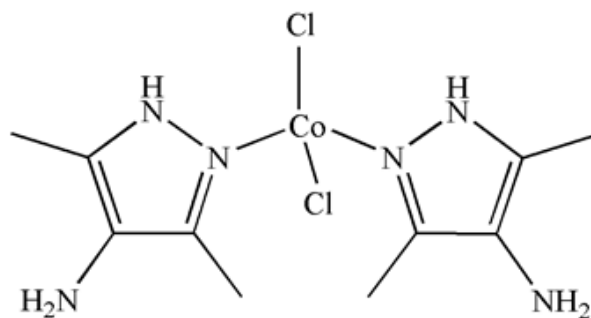


M = Cu, Co, Ni, Zn, Mn

X = NO_3^- , Cl^- , ClO_4^- , CH_3COO^-

Solvents = H_2O , CH_3OH , DMF

The formation of the title compound proceeds according to the following reaction Scheme 2.



Scheme 2. Formation of the title compound $[Co(C_5H_9N_3)_2Cl_2]$.

To confirm the fact of coordination of the ligand to the metal ion, an IR study of the obtained complex $[Co(C_5H_9N_3)_2Cl_2]$ was compared with the spectra of the ligand. (Figure 1).

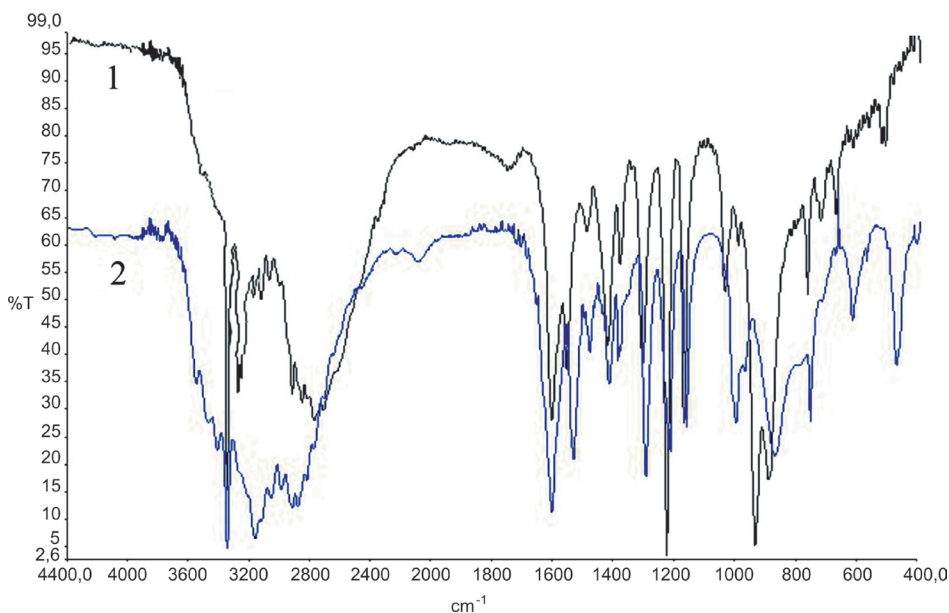


Fig. 1. IR spectra of complex $[Co(C_5H_9N_3)_2Cl_2]$ (1) and 3,5-dimethyl-4-amino-1H-pyrazole (2).

In the comparative analysis of the IR spectra of the synthesized complex and ligand, the main attention was paid to the absorption bands corresponding to the oscillations of the functional groups of the ligand. Accordingly, in the IR spectra of $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$ and 3,5-dimethyl-4-amino-1H-pyrazole observed an intense sharp band of the valence oscillations of $\nu(\text{NH})$ in the region of 3350 cm^{-1} (for complex), 3347 cm^{-1} (for L). Both spectra have several bands in the region of $2880\text{--}3280\text{ cm}^{-1}$ corresponding to the asymmetric and symmetric stretch of $\nu(\text{NH}_2)$; scissoring oscillations of (NH_2) for complex 1561 cm^{-1} , for 3,5-dimethyl-4-amino-1H-pyrazole – 1537 cm^{-1} . There are several bands in the region of $2700\text{--}2900\text{ cm}^{-1}$ corresponding to the oscillations of $\nu(\text{CH}_3)$ asymmetric and symmetric stretch, in the region of $1386\text{--}1427\text{ cm}^{-1}$ of $\rho(\text{CH}_3)$ asymmetric and symmetric stretch. A rather intense and sharp peak in the region of 1232 cm^{-1} (for complex) and 1299 cm^{-1} (for L) indicates the presence of $\nu(\text{C-N})$ oscillations. A band is pre-

sent in the absorption region of $\nu(\text{C=N})$ oscillations: 1609 cm^{-1} (for complex) and 1607 cm^{-1} (for L) [19]. In view of the above facts, it can be stated indicating the presence of a coordinated but not deprotonated ligand.

The electronic spectra of the title compound (Figure 2, B) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Figure 2, A) in the same solvent (methanol solution) indicate absorption maxima at 600 and 670 nm for $\text{CoCl}_2 \cdot \text{H}_2\text{O}$, and at 600 and 650 nm for the complex. The first of these bands in each case appear as shoulders and may be attributed to charge transfer from the ligand to cobalt, and the second can be assigned as the d–d transitions of cobalt(II) ions. During complex formation, the most intense band is shifted to the short-wavelength region by 20 nm in comparison with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Since the expected data for octahedral cobalt complexes are 400–500 nm (chromophore $\text{CoO6} - \text{CoN6}$), and for tetrahedral complexes are 600–700 nm (chromophore CoN4), the results suggest the tetrahedral structure of the obtained complex [20].

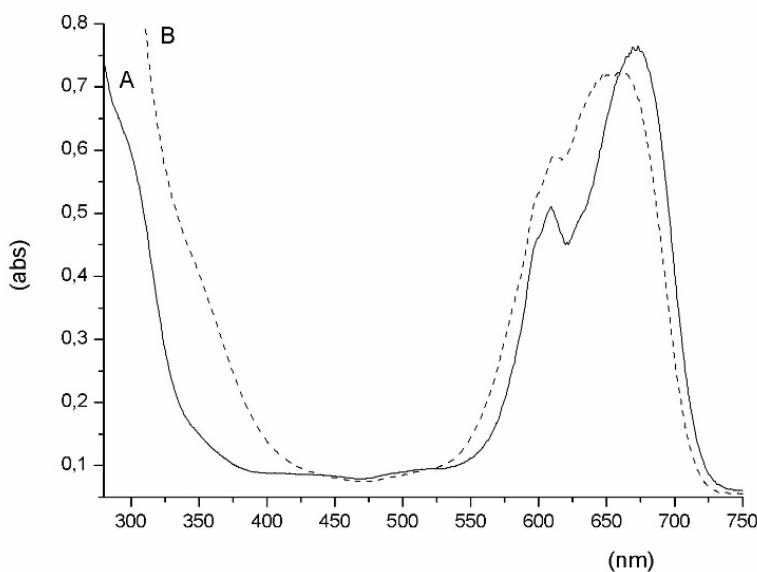


Fig. 2. Absorbance (methanol solution) electronic spectra of the title compound (B) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (A).

In the title compound, 3,5-dimethyl-4-amino-1H-pyrazole is a neutral ligand bound to cobalt ion *via* the pyridine-type nitrogen atom thus providing the formation of the mononuclear complex (Figure 3).

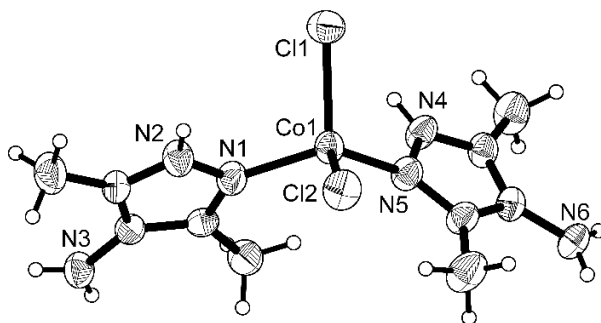


Fig. 3. The molecular structure of $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$, shows the atom-numbering scheme and the cobalt coordination environment. Displacement ellipsoids are drawn at the 50% probability level.

The Co as the central atom has a tetrahedral coordination environment formed by two nitrogen atoms belonging to the two 3,5-dimethyl-4-amino-1H-pyrazole ligands [$\text{Co1-N1} = 2.005(3)$ and $\text{Co1-N5} = 2.006(3)$ Å] and two chlorine atoms [$\text{Co1-Cl2} = 2.2400(11)$ and $\text{Co1-Cl1} = 2.2863(12)$ Å] (Table 2). The bond lengths Co–N (varying in the range of $2.001(0) - 2.049(0)$ Å) and Co–Cl (varying in the range of $2.222(0) - 2.252(0)$ Å) for similar compounds were found in the literature [21, 22]. Hence, the distances Co–N and Co–Cl of the title complex are typical.

Table 2.

Selected bond lengths (Å) and bond angles (deg) of $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$. Symmetry codes: (i: $-1+x, y, z$; ii: $-1-x, 1-y, 2-z$).

Co1–N1	2.007(3)
Co1–N5	2.008(3)
Co1–Cl1	2.2861(13)

Co1–Cl2	2.2404(12)
N2 ⁱⁱ –H2 ⁱⁱ ...N6	2.859(14)
N4 ⁱ –H4 ⁱ ...N3 ⁱⁱ	2.942(7)
N6–H6A...Cl1	2.736(6)
N3–H3B...Cl1	2.791(11)
C6–H6C...Cl2	2.713(4)
Cl1–Co1–N5	103.65(11)
Cl1–Co1–N1	104.88(11)
Cl1–Co1–Cl2	114.21(5)
N1–Co1–N5	116.00(14)
$\angle \text{N2}^{\text{ii}}\text{--H2}^{\text{ii}}\text{...N6}$	175.09(27)
$\angle \text{N4}^{\text{i}}\text{--H4}^{\text{i}}\text{...N3}^{\text{ii}}$	163.51(23)
$\angle \text{N6--H6A...Cl1}$	171.14(26)
$\angle \text{N3--H3B...Cl1}$	133.02(26)
$\angle \text{C6--H6C...Cl2}$	148.61(36)

In the crystal packing (Figure 4) the molecules of complex $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$ are connected through intermolecular hydrogen bonds (N2-H2...N6 , N4-H4...N3 , N3-H3B...Cl1 , N6-H6A...Cl1) hydrogen bonds in the two-dimensional polymer. The hydrogen bonds N–H...N are formed by N, H atoms of NH- and NH₂-groups from 3,5-dimethyl-4-amino-1H-pyrazole. Additionally, NH₂-group forms the intermolecular hydrogen bonds with the chlorine atoms (N6-H6A...Cl1 , N3-H3B...Cl1). The non-classical intramolecular hydrogen bonds between the chloride anions and CH₃-groups of the ligand (C6-H6C...Cl2) are also present in the crystal packing of the complex $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$.

Due to such organization of crystal packing the intermolecular hydrogen bonds N–H...N take part in forming the sixteen- and twenty-membered cycles, which are interchangeable in the molecular structure. The four mo-

lecules of the ligand with two Co atoms are connected by hydrogen bonds $N4-H4\cdots N3$ and take part in forming the sixteen-membered cycle. The interchangeable hydrogen bonds $N2-H2\cdots N6$ and $N4-H4\cdots N3$ from four

molecules of the ligand take part in the formation of the twenty-membered cycle. In the crystal packing the shortest intrachain Co...Co separations are 7.407(27) Å.

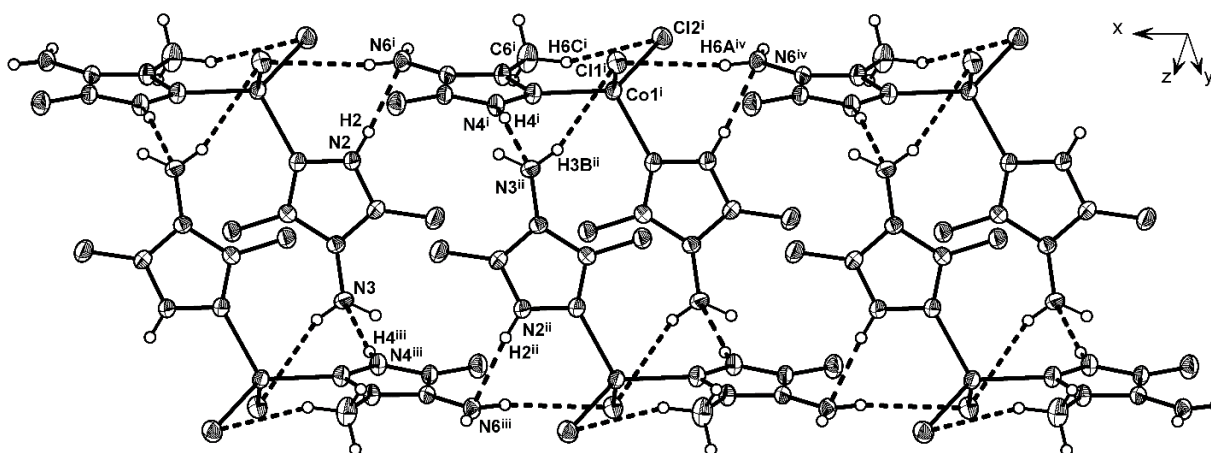


Fig. 4. A crystal packing diagram of the complex $[Co(C_5H_9N_3)_2Cl_2]$ shows hydrogen bonds as underlined dotted lines and shaded black, which link the molecules of the title compound in the two-dimensional polymer.

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

The Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were performed using Crystal Explorer 17.5 software [23], with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed color scale of -0.6232 (red) to 1.6217 (blue) a.u. There are 12 red spots on the d_{norm} surface (Figure 5).

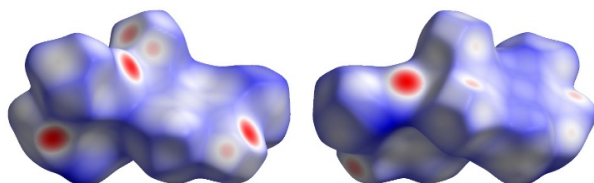


Fig. 5. Two projections of Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule.

The dark-red spots arise as a result, of short interatomic contacts and represent negative d_{norm} values on the surface, while the other weaker intermolecular interactions appear as light-red spots. The Hirshfeld surfaces mapped over d_{norm} are shown for the $H\cdots H$, $H\cdots Cl/Cl\cdots H$, $H\cdots N/N\cdots H$ and $H\cdots C/C\cdots H$ contacts, the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Figure 6.

All short interatomic contacts are in the range of $1.829\text{--}2.782$ Å. The shortest contacts are $NH\cdots N$ and the longest contacts are $NH\cdots Cl$. The most significant contributions to the overall crystal packing are from $H\cdots H$ (47.1%), $H\cdots Cl/Cl\cdots H$ (28.5%), $H\cdots N/N\cdots H$ (12.9%) and

H...C/C...H (9.7%) contacts. The small contribution of the other weak intermolecular C...Cl/Cl...C (0.7%), C...C (0.4%), H...Co/Co...H (0.3%), C...N/N...C (0.2%), C...Co/Co...C (0.1%) and Cl...Cl (0.1%) contacts has a negligible ef-

fect on the packing. Also, quantitative physical properties of the Hirshfeld surface for this compound were obtained, such as molecular volume ($377.18 \text{ \AA}^3$), surface area ($345.22 \text{ \AA}^2$), globularity (0.731), as well as asphericity (0.154).

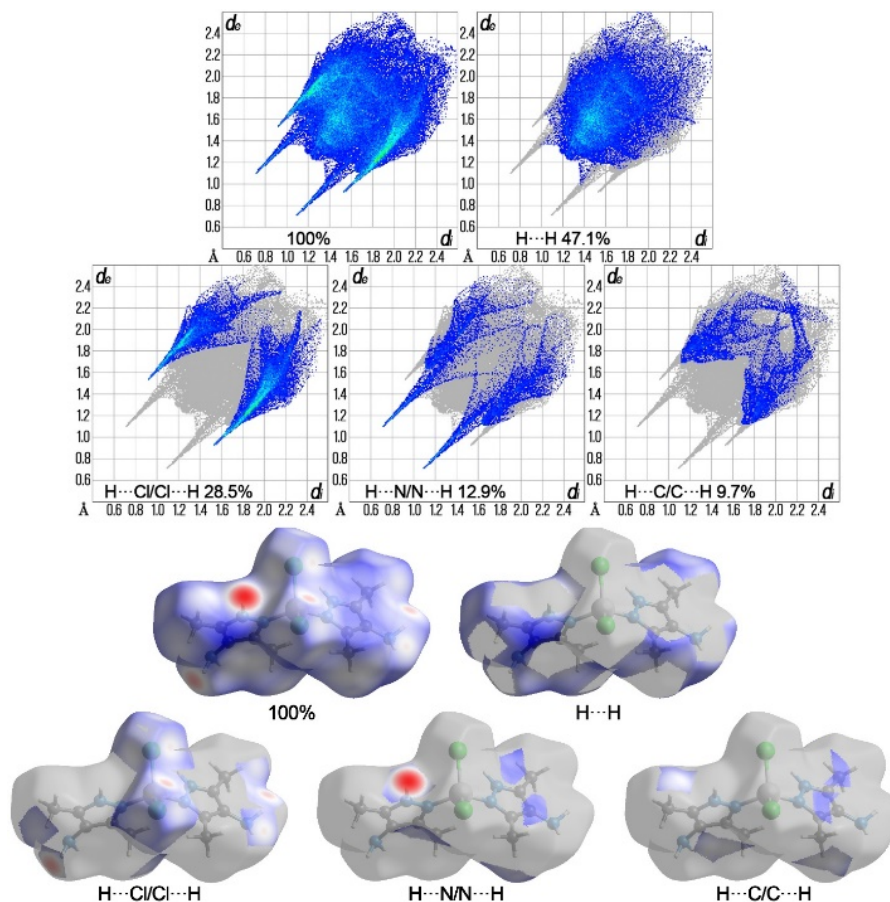


Fig. 6. The overall two-dimensional fingerprint plot and those delineated into specified interactions. Hirshfeld surface representations with the function d_{norm} plotted onto the surface for the different interactions.

CONCLUSIONS. The present work describes the synthesis and characterization of the mononuclear coordination compound $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$. X-ray analysis of the complex reveals that the cobalt atom has a tetrahedral coordination environment formed by two nitrogen atoms belonging to the two 3,5-dimethyl-4-amino-1H-pyrazole and two chlorine

atoms. In the crystal structure the molecules are linked through intermolecular hydrogen bonds ($\text{N}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{Cl}$) and non-classical intramolecular hydrogen bonds ($\text{C}-\text{H}\cdots\text{Cl}$). It was found that the introduction to the 4th position of the 3,5-dimethyl-1H-pyrazole NH_2 group does not contribute to the participation of the latter in coordination. The reason for this

fact may be the weak σ -donor capacity of the NH_2 group in the pyrazole cycle. Hirshfeld surface analysis was used to study intermolecular interactions in the crystal. The 2D-fingerprint plot calculations displayed the $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ contacts that were the most significant interaction with the Hirshfeld surface.



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СИНТЕЗ, КРИСТАЛІЧНА СТРУКТУРА, СПЕКТРАЛЬНІ ХАРАКТЕРИСТИКИ ТА АНАЛІЗ ПОВЕРХНІ ХІРШФЕЛЬДА КОМПЛЕКСУ ДИХЛОРО-БІС(3,5-ДИМЕТИЛ-4-АМІНО-1Н-ПІРАЗОЛ) КОБАЛЬТУ(II)

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Синтезовано та охарактеризовано методами ЕСП, ІЧ-спектроскопії моноядерний комплекс Co(II) на основі 3,5-диметил-4-аміно-1Н-піразолу. Методом РСТА встановлено молекулярну будову отриманої в кристалічному стані сполуки $[\text{Co}(\text{C}_5\text{H}_9\text{N}_3)_2\text{Cl}_2]$, в якій атом кобальту знаходиться у викривленому тетраедричному оточенні N_2Cl_2 , що сформоване завдяки координації атомів хлору [$\text{Co1}-\text{Cl2} = 2.2400(11)$ і $\text{Co1}-\text{Cl1} = 2.2863(12)$ Å] та піридинових атомів азоту від двох недепротоно-

ваних монодентатно координованих молекул ліганду [$\text{Co1}-\text{N1} = 2.005(3)$ і $\text{Co1}-\text{N5} = 2.006(3)$ Å]. Наведено синтез 3,5-диметил-4-аміно-1Н-піразолу, а також характеристику ліганду за допомогою ЯМР, ІЧ-спектроскопії та елементного аналізу. Кристалічна структура моноядерного комплексу додатково застіблізована міжмолекулярними водневими зв'язками ($\text{N}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{Cl}$) та некласичними внутрішньомолекулярними водневими зв'язками ($\text{C}-\text{H}\cdots\text{Cl}$). Аналіз поверхні Хіршфельда показав, що найбільш важливий внесок у кристалічну упаковку вносять міжмолекулярні $\text{H}\cdots\text{H}$ (47.1%) та $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ (28.5%) контакти.

Ключові слова: піразол, комплекс кобальту, кристалічна структура, РСТА, аналіз поверхні Хіршфельда.

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