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Four new Co(II) complexes with 2-amino-4-methylpyridine, 2-amino-3-methylpyridine, or 2-amino-5-chloropyridine: synthesis, spectroscopy, magnetic properties, and crystal structure

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Solid-state structures for a series of $[\text{Co}(\text{L})_2\text{X}_2]$ complexes are assigned on the basis of magnetic moments, FTIR spectra, electronic spectra properties (L = 2-amino-4-methylpyridine, 2-amino-3-methylpyridine, or 2-amino-5-chloropyridine; X = chloride or acetate). All complexes were prepared in one-step syntheses. The crystal structure of 2-amino-4-methylpyridine with cobalt(II) chloride $[\text{Co}(\text{L})_2(\text{Cl})_2]$ was solved at room temperature. This compound consists of mononuclear units consisting of two ligands linked to cobalt *via* the pyridine. The complex crystallizes in the orthorhombic system, space group *Pcan* with $z = 8$. UV-Vis spectra show five absorption bands, attributed to d–d transitions of cobalt, ligand → metal charge transfer, and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of ligand. FTIR spectra show CoL_2X_2 vibrations at $550\text{--}300\text{ cm}^{-1}$. The compounds show room temperature magnetic moments of 4.58–5.29 B.M., indicating high-spin cobalt(II).

Keywords: Cobalt(II) complexes; Crystal structure of cobalt(II); Magnetic moment of cobalt(II)

1. Introduction

Cobalt(II) complexes are important in biology mainly because of coenzyme B_{12} [1]. A report of insulin-like action of cobalt(II) chloride implies that such metal complexes may have similarities with vanadium compounds, which exhibit insulin-like effects [2–9]. Electronic properties of cobalt(II) compounds have received substantial attention [10–12] in part due to the fact that many of these complexes bind oxygen reversibly [13] and are model systems for vitamin B_{12r} . Cobalt is a necessary trace element in mammals and has many uses in medicine, magnetic resonance imaging, and drug delivery [14]. Cobalt ethylenediamine complexes are

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potent anti-microbial agents [15]. Low-spin cobalt(II) porphyrins [16, 17] are of interest since cobalt-substituted hemoglobin, "coboglobin", binds oxygen in a cooperative fashion [18]. The growth of cobalt(II) chemistry has necessitated the development of models to account for and predict the spectroscopic properties of cobalt(II) complexes. Cobalt(II) compounds have interesting magneto-chemistry, as shown in a recent review on magnetic metal-organic frameworks [19]. Strong magnetic anisotropy of high-spin cobalt(II) is at the origin of the increasing interest in polynuclear compounds containing this metal ion [20]. Several examples of high-nuclearity complexes with six-coordinate cobalt(II) behaving as single molecule magnets and single chain magnets have been reported [21–24]. Among the different bridging ligands explored, carboxylate is appealing because of the different conformations that it can adopt (*syn-syn*, *anti-syn*, and *anti-anti*) and its ability to mediate ferro- or antiferromagnetic interactions between paramagnetic centers, as illustrated by carboxylate-bridged copper(II) complexes [25, 26]. A few magneto-structurally characterized examples of complexes with carboxylate-bridged, high-spin cobalt(II) are known where weak antiferromagnetic interactions across the *syn-syn* conformation [27] and either ferro- or antiferromagnetic interactions through the *anti-anti* [28] and *anti-syn* [29] conformations occur. Electronic spectra of cobalt(II) complexes CoX_4 , CoA_3B , and CoA_2B_2 (X, A, B = monodentate ligands) of tetrahedral, pseudo-tetrahedral C_{3v} , and pseudo-tetrahedral C_{2v} , respectively, have been studied [30–32] with three $d \rightarrow d$ transitions between 5×10^3 and $20 \times 10^3 \text{ cm}^{-1}$. The two lower energy absorptions correspond to the ^4F term (in tetrahedral symmetry), while the highest one arises from the 4P free ion term [33–35]. We have been interested in cobalt(II) complexes with 2-amino-4-methylpyridine, 2-amino-3-methylpyridine, or 2-amino-5-chloropyridine as ligands. Such complexes have potential for antibacterial activities and we will focus on this subject in the future. The complexes were synthesized in a one-step synthesis and characterized by elemental analysis, Fourier transform infrared (FTIR), electronic spectra, room temperature magnetic moments, and a crystal structure.

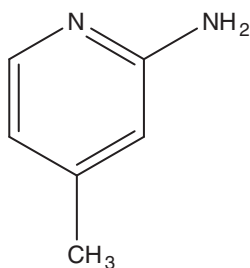
2. Experimental

2.1. Chemicals

All chemicals of reagent grade quality were purchased from Merck Chemical Company and used as received.

2.2. Physical measurements

C, H, and N determinations were undertaken using an Elementar Analysis System GmbH Vario EL II. Cobalt was determined on a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer operating at 240.7 nm. Electronic spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using diffuse reflectance with MgO as a reference. FTIR spectra were obtained from 4000 to 300 cm^{-1} as KBr discs using a Galaxy series FTIR 5000 spectrophotometer. Spectra were calibrated using polystyrene bands at 3028, 1601, and 1208 cm^{-1} . The room temperature magnetic moment of each



Scheme 1. Structure of 2-amino-4-methylpyridine.

complex was measured according to the Evans method [36]. ^1H NMR determination was carried out on a Bruker 300 MHz spectrometer.

2.3. Crystal structure determination and refinement

Single-crystal data were collected on a STOE IPDS-II diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The green-bluish block crystal of $0.2 \times 0.15 \times 0.05 \text{ mm}^3$ was mounted on a glass fiber for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 4198 unique reflections. Data were collected at 298(2) K to a maximum 2θ value of 29.24° in a series of ω scans in 1° oscillations and integrated using the STOE X-Area [37] software package. The numerical absorption coefficient, μ , for Mo-K α radiation is 1.441 mm^{-1} . A numerical absorption correction was applied using X-RED [38] and X-SHAPE [39] software. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [40] and subsequent difference Fourier maps and then refined on F^2 by full-matrix least-squares using anisotropic displacement parameters [41]. All hydrogens were located in a difference Fourier map and then refined isotropically. Subsequent refinement converged with R factors and parameter errors significantly better than for all attempts to model the solvent disorder. All refinements were performed using X-STEP32 crystallographic software package [42]. A summary of the crystal data, experimental details and refinement results is given in table 1.

2.4. Preparation of the complexes

The coordination compounds were prepared according to the following general procedure:

[Co(2-amino-4-methylpyridine) $_2$ (Cl) $_2$] (1): Two millimolar cobalt(II) chloride dihydrate and 4.1 mmol 2-amino-4-methylpyridine (scheme 1) were each dissolved in 25 mL methanol. The Co(II) solution was then slowly added to the ligand solution. After 1 week, the blue precipitate was collected and washed with methanol and diethyl ether. Yield *ca* $\approx 70\%$. Elemental analysis for $\text{CoC}_{12}\text{H}_{16}\text{N}_4\text{Cl}_2$ (1): Found (%): C, 41.95; H, 4.43; N, 15.43; Co, 17.04. Calcd (%): C, 41.60; H, 4.62; N, 16.10; Co, 16.93.

Table 1. Crystallographic and structure refinement data for [Co(2-amino-4-methylpyridine)₂(Cl)₂].

Empirical formula	CoC ₁₂ H ₁₆ N ₄ Cl ₂
Formula weight	346.12
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pcan</i>
Crystal size (mm ³)	0.2 × 0.15 × 0.05
Unit cell dimensions (Å, °)	
<i>a</i>	8.6016(4)
<i>b</i>	14.3561(7)
<i>c</i>	25.1483(17)
α	90
β	90
γ	90
Volume (Å ³), <i>Z</i>	3105.4(3), 8
Calculated density (Mg m ⁻³)	1.481
Absorption coefficient (mm ⁻¹)	1.441
<i>F</i> (000)	1416
Crystal size (mm ³)	0.2 × 0.15 × 0.05
θ range for data collection	2.15–29.24
Index ranges	–11 ≤ <i>h</i> ≤ 10; –19 ≤ <i>k</i> ≤ 19; –34 ≤ <i>l</i> ≤ 34
Reflection collected/unique	33011/4198 [<i>R</i> (int) = 0.10691]
Completeness to $\theta = 29.24$ (%)	99.2
Absorption correction	Numerical
Max and min. transmission	0.933 and 0.775
Refinement method	Full matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4198/0/188
Goodness-of-fit on <i>F</i> ²	1.103
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0679, <i>wR</i> ₂ ^a = 0.1097
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1238, <i>wR</i> ₂ ^a = 0.1273
Largest difference peak and hole (e Å ⁻³)	0.325 and –0.276

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (wF_o^2)^2]^{1/2}.$$

[Co(2-amino-5-chloropyridine)₂Cl₂] (2): Two millimolar of cobalt(II) chloride dihydrate and 4.1 mmol of 2-amino-5-chloropyridine were each dissolved in 25 mL of methanol. The Co(II) solution was then slowly added to the ligand solution, preventing precipitation, and the solution was filtered. After the solution stood for 5 days, the product separated. Yield *ca* ≈ 82%. Elemental analysis for CoC₁₀H₁₀N₄Cl₄ (2): Found (%): C, 30.94; H, 2.81; N, 14.17; Co, 15.17. Calcd (%): C, 31.02; H, 2.50; N, 14.46; Co, 15.24.

[Co(2-amino-3-methylpyridine)₂Cl₂] (3): Two millimolar of cobalt(II) chloride dihydrate and 4.1 mmol of 2-amino-3-methylpyridine were each dissolved in 25 mL of CH₃OH. The Co(II) solution was then added slowly to the ligand solution and the solution was filtered. After the solution stood for 2 weeks, the product separated. Yield *ca* ≈ 84%. Elemental analysis for CoC₁₂H₁₆N₄Cl₂ (3): Found (%): C, 42.57; H, 4.46; N, 17.09; Co, 17.45. Calcd (%): C, 41.60; H, 4.62; N, 16.10; Co, 16.93%.

[Co(2-amino-4-methylpyridine)₂(acetate)₂] (4): Two millimolar of cobalt(II) acetate and 4.1 mmol of 2-amino-4-methylpyridine were each dissolved in 25 mL of CH₃CN. The Co(II) solution was slowly added to the ligand solution, preventing precipitation, and the solution was filtered. After the solution stood for 2 weeks, the product separated. Yield *ca* ≈ 78%. Elemental analysis for CoC₁₆H₂₂N₄O₄ (4): Found (%): C, 49.27; H, 5.70; N, 14.50; Co, 14.80. Calcd (%): C, 48.89; H, 5.59; N, 14.28; Co, 15.00.

Table 2. Spectroscopic data for all complexes.

Complex	Absorption UV-Vis ($\times 10^3 \text{ cm}^{-1}$)	IR (Co-N) (Co-Cl) (Co-O) (cm^{-1})	μ_{Co} (R.T.) B.M.
1	15.7, 16.3, 17.2, 36.2, 41.8	551, 472, 322, 300	4.58
2	15.6, 16.0, 18.9, 33.6, 40.7	5.22, 466, 435, 343	4.83
3	15.7, 16.1, 17.2, 37.0, 41.7	474, 434, 376, 327	5.04
4	17.5, 18.9, 20.8, 35.1, 41.3	540, 490, 476, 399	5.29

3. Results and discussion

3.1. Electronic spectra

Spectroscopic data for all complexes are presented in table 2; complexes **1**, **2**, and **3** are very similar to each other, typical for tetrahedral cobalt(II) complexes as shown by X-ray analysis for **1**. The spectrum for **2** is slightly higher in intensity than **1** and **3**, perhaps indicating that the coordination geometry around cobalt(II) in **2** is more distorted than that in **1** and **3** [43, 44]. Electronic structures of cobalt(II) complexes with different ligands have been presented [17, 43, 45]. On the basis of the simplest model three spin-allowed bands are expected in tetrahedral cobalt(II) complexes, i.e., ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$. Usually such complexes show two bands between 12×10^3 and $16 \times 10^3 \text{ cm}^{-1}$, which can be assigned to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$, respectively; ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ is usually observed as a well-defined shoulder at $18 \times 10^3 \text{ cm}^{-1}$ [44]. The electronic spectra of **1–4** were obtained from solid samples using diffuse reflectance. The compounds show a broad shoulder with bands at (15.7×10^3 , 16.3×10^3 , and $17.2 \times 10^3 \text{ cm}^{-1}$), (15.6×10^3 , 16.0×10^3 , and $18.9 \times 10^3 \text{ cm}^{-1}$), (15.7×10^3 , 16.1×10^3 , and $17.2 \times 10^3 \text{ cm}^{-1}$), and (17.5×10^3 , 18.9×10^3 , and $20.8 \times 10^3 \text{ cm}^{-1}$) for **1–4**, respectively [43, 44]. Absorptions at 36.2×10^3 , 33.6×10^3 , 37.0×10^3 , and 35.1×10^3 for **1–4**, respectively, are associated to charge transfer from the non-bonding orbital of chloride or oxygen to half-field d orbitals of cobalt(II) [44, 46]. The absorption band at $41.5 \times 10^3 \text{ cm}^{-1}$ is assigned with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [47, 48].

3.2. Infrared spectra

Spectra of the free ligands and complexes were obtained from 4000 to 300 cm^{-1} . All bands present in the free ligand are also observed in the spectra of the complexes. Based on data from earlier reports, we assign bands at 551 and 472, 522 and 466, and 474 and 434 cm^{-1} for **1**, **2**, and **3**, respectively, to Co–N vibrations. Co–Cl vibrations for **1**, **2**, and **3** are assigned to 322 and 300, 435, and 343, and 376 and 327 cm^{-1} , respectively. Bands at 540 and 490 cm^{-1} can be assigned to Co–O vibrations. Bands at 476 and 399 cm^{-1} are attributed to Co–N vibrations for **4** [49–51].

3.3. Magnetic moment

The magnetic moments of all complexes were determined by the Evans method [36]. This method is based on the principle that the position of a given proton resonance (*t*-butyl alcohol) in the spectrum of a molecule is dependent on the bulk susceptibility of the medium in which the molecule is found (Supplementary material). The shift of a

proton resonance line of an inert substance due to the presence of paramagnetic ions is given by theoretical expression (1):

$$\Delta\nu/\nu_0 = (2\pi/3)(\chi_\nu - \chi_{\nu'}), \quad (1)$$

where $\Delta\nu$ is the shift, ν_0 is the applied field, χ_ν is the volume susceptibility of the solution containing paramagnetic ions, and $\chi_{\nu'}$ is the volume susceptibility of the reference solution. All complexes at room temperature have magnetic moment between 4.58 and 5.29 B.M., agreeing well with high-spin $3d^7$ configuration for cobalt(II) [52]. As seen in table 2, an electron donor on pyridine decreases the magnetic moment, while a withdrawing group increases the magnetic moment [53].

3.4. Description of the crystal structure of 1

The solid-state structure of **1** determined by single-crystal X-ray diffraction, together with atom labeling, is shown in figure 1. Crystallographic data and structure refinement parameters are summarized in table 1. Selected bond lengths and angles with estimated standard deviations are given in table 3. Hydrogen bonds and angles are presented in table 4 and torsion angles in ‘‘Supplementary material’’. An ORTEP view of the complex is shown in figure 2. The structure consists of a cobalt surrounded by two ligands and two chlorides. Co–N distances are 2.03 Å and Co–Cl 2.25 Å. The angles N(3)–Co–Cl(2) and N(3)–Co–Cl(1) are 109°, while the N(1)–Co–Cl(1) and N(1)–Co–Cl(2) angles are 104° and 115°, respectively. N(1)–Co–N(3) and Cl(1)–Co–Cl(2) angles are 104° and 112°, respectively, indicating a distorted tetrahedral structure for cobalt(II). Four-coordinate cobalt(II) species with two different ligands are almost invariably distorted from regular tetrahedral symmetry from a coupling between electronic and vibration wave functions that lowers the ground-state energy [54].

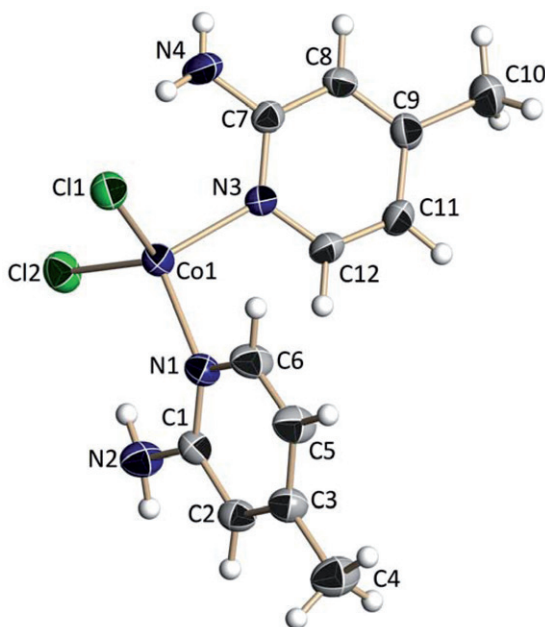


Figure 1. Crystal structure of $[\text{Co}(\text{2-amino-4-methylpyridine})_2(\text{Cl})_2]$.

Table 3. Bond lengths (Å) and angles (°) for [Co(2-amino-4-methylpyridine)₂(Cl)₂].

C(1)–N(1)	1.344(4)	C(1)–N(2)	1.352(5)	C(1)–C(2)	1.398(5)
C(2)–N(3)	1.366(5)	C(2)–H(2)	0.9300	C(3)–C(5)	1.395(6)
C(3)–C(4)	1.506(5)	C(4)–H(4A)	0.9600	C(4)–H(4B)	0.9600
C(6)–N(1)	1.365(5)	C(6)–H(6)	0.9300	C(7)–N(4)	1.352(5)
C(7)–N(3)	1.357(4)	C(7)–C(8)	1.387(5)	C(8)–C(9)	1.357(5)
C(8)–H(8)	0.9300	C(9)–C(11)	1.400(5)	C(9)–C(10)	1.506(6)
C(10)–H(10A)	0.9600	C(10)–H(10B)	0.9600	C(10)–H(10C)	0.9600
C(11)–C(12)	1.345(5)	C(11)–H(11)	0.9300	C(12)–N(3)	1.342(5)
C(12)–H(12)	0.9300	N(1)–Co(1)	2.030(3)	N(2)–H(2B)	0.88(4)
N(2)–H(2C)	0.88(5)	N(3)–Co(1)	2.035(3)	N(4)–H(4D)	0.77(4)
N(4)–H(4E)	0.80(5)	Co(1)–Cl(2)	2.2483(11)	Co(1)–Cl(1)	2.2512(11)
N(1)–C(1)–N(2)	117.9(3)	N(1)–C(1)–C(2)	121.9(3)	–	–
N(2)–C(1)–C(2)	120.1(3)	C(3)–C(2)–C(1)	120.5(3)	–	–
C(2)–C(3)–C(5)	117.5(4)	C(2)–C(3)–C(4)	121.8(4)	–	–
C(5)–C(3)–C(4)	120.7(4)	C(3)–C(4)–H(4A)	109.5	–	–
C(3)–C(4)–H(4B)	109.5	H(4A)–C(4)–H(4B)	109.5	–	–
C(3)–C(4)–H(4C)	109.5	H(4A)–C(4)–H(4C)	109.5	–	–
H(4B)–C(4)–H(4C)	109.5	C(6)–C(5)–C(3)	119.7(4)	–	–
C(6)–C(5)–H(5)	120.2	C(3)–C(5)–H(5)	120.2	–	–
C(5)–C(6)–N(1)	123.8(4)	C(5)–C(6)–H(6)	118.1	–	–
N(1)–C(6)–H(6)	18.1	N(4)–C(7)–N(3)	117.1(4)	–	–
N(4)–C(7)–C(8)	121.2(4)	N(3)–C(7)–C(8)	121.6(3)	–	–
C(9)–C(8)–C(7)	120.4(3)	C(9)–C(8)–H(8)	119.8	–	–
C(7)–C(8)–H(8)	119.8	C(8)–C(9)–C(11)	117.6(3)	–	–
C(8)–C(9)–C(10)	122.1(4)	C(11)–C(9)–(10)	120.3(4)	–	–
C(9)–C(10)–N(10A)	109.5	C(9)–C(10)–N(10B)	109.5	–	–
H(10A)–C(10)–H(10B)	109.5	C(9)–C(10)–H(10C)	109.5	–	–
H(10A)–C(10)–H(10C)	109.5	H(10B)–C(10)–H(10C)	109.5	–	–
C(12)–C(11)–C(9)	119.4(4)	C(12)–C(11)–H(11)	120.3	–	–
C(9)–C(11)–H(11)	120.3	N(3)–C(12)–C(11)	124.0(3)	–	–
N(3)–C(12)–H(12)	118.0	C(11)–C(12)–H(12)	118.0	–	–
C(1)–N(1)–C(6)	116.6(3)	C(1)–N(1)–Co(1)	129.1(2)	–	–
C(6)–N(1)–Co(1)	114.1(2)	C(1)–N(2)–H(2B)	117(2)	–	–
C(1)–N(2)–H(2C)	112(3)	H(2B)–N(2)–H(2C)	122(4)	–	–
C(12)–N(3)–C(7)	116.9(3)	C(12)–N(3)–Co(1)	117.5(2)	–	–
C(7)–N(4)–H(4E)	117(3)	H(4D)–N(4)–H(4E)	127(5)	–	–
N(1)–Co(1)–N(3)	104.61(11)	N(1)–Co(1)–Cl(2)	115.26(8)	–	–
N(3)–Co(1)–Cl(2)	109.27(8)	N(1)–Co(1)–Cl(1)	104.82(9)	–	–
N(3)–Co(1)–Cl(1)	109.91(9)	Cl(2)–Co(1)–Cl(1)	112.58(5)	–	–

Table 4. Hydrogen bonds (Å) and angles (°) for [Co(2-amino-4-methylpyridine)₂(Cl)₂].

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)	Symmetry codes
N2–H2B...Cl2	0.89(4)	2.52(4)	3.350(4)	157 (3)	<i>x</i> , <i>y</i> , <i>z</i>
N2–H2C...Cl1	0.89(6)	2.53(6)	3.403(4)	170 (4)	1/2+ <i>x</i> , 1/2– <i>y</i> , <i>z</i>
N4–H4D...Cl2	0.77(4)	2.68(4)	3.409(5)	159 (4)	<i>x</i> , 1– <i>y</i> , 1/2– <i>z</i>
N4–H4E...Cl1	0.81(5)	2.67(5)	3.418(5)	154 (4)	<i>x</i> , <i>y</i> , <i>z</i>
C10–H10C...Cl2	0.9600	2.8100	3.763(5)	171	1/2+ <i>x</i> , 1/2+ <i>y</i> , 1/2– <i>z</i>

4. Conclusion

Four new cobalt(II) complexes with 2-amino-4-methylpyridine, 2-amino-3-methylpyridine, or 2-amino-5-chloropyridine have been made in one-step synthesis and

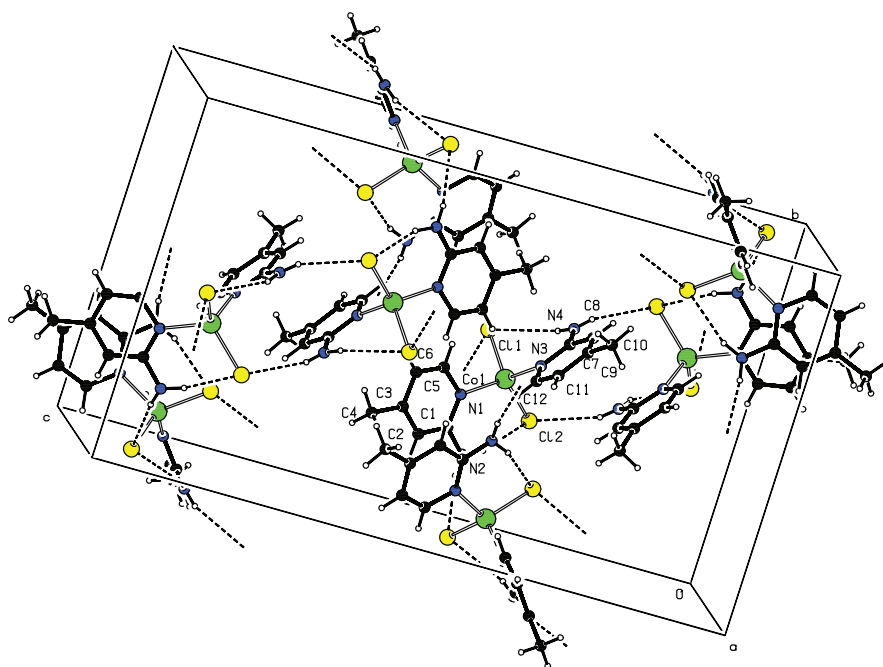


Figure 2. ORTEP view of $[\text{Co}(\text{2-amino-4-methylpyridine})_2(\text{Cl})_2]$.

spectroscopically characterized. The UV-Vis spectra show five absorption bands, attributed to d-d transitions of cobalt, ligand \rightarrow metal charge transfer, and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of ligand. The FTIR spectra show CoL_2X_2 unit vibrations in the range $550\text{--}300\text{ cm}^{-1}$. All complexes at room temperature have magnetic moments between 4.58 and 5.29 B.M., agreeing with high-spin $3d^7$ configuration for cobalt(II). The complexes of cobalt(II) with the above ligand have potential antibacterial activities, and this will be our future research subject.

Supplementary material

CCDC 804552 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

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