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Synthesis, Spectroscopy, and Magnetic Characterization of Copper(II) and Cobalt(II) Complexes with 2-Amino-5-Bromopyridine as Ligand[1]

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Abstract—The synthesis, spectroscopic, and magnetic characterization of two new copper(II) and cobalt(II) complexes are described. Both two compounds have the general formula $[M(L)_2(Cl)_2]$ (M = Cu (**I**), Co (**II**); L = 2-amino-5-bromopyridine). These complexes were prepared in one-step synthesis and characterized by elemental analysis, FT-IR, UV-Vis, and EPR spectroscopy. Moreover, the single crystal structure of complex **I** was studied by the X-ray diffraction method. This compound consists of mononuclear units consisting of two ligands linked to metal via the nitrogen of pyridine ring. The UV-Vis spectra of copper(II) and cobalt(II) complexes show three and five absorption bands, respectively, attributed to the *d–d* transition of the metal ion, ligand → metal charge transfer and $\pi \to \pi^*$ or $n \to \pi^*$ transitions of the ligand. The FT-IR spectra show MN_2Cl_2 vibrations at 500–300 cm^{-1}. The complexes show room temperature magnetic moments of 1.78 and 4.12 μ_B for Cu(II) and Co(II), respectively. The X-band electron spin resonance (ESR) spectra of Cu(II) complex in DMF or DMSO frozen at liquid nitrogen temperature show the typical $\Delta M_S = \pm 1$ transition.

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INTRODUCTION

The study of transition metal ion complexes by magnetic and optical techniques has furnished a considerable body of empirical data, much of which can be understood in terms of the phenomenological ligand field theory [1]. The major portion of this data is primarily concerned with complexes containing a single paramagnetic transition metal ion; relatively little information is available on dimeric and trimeric coordination complexes [2]. Since copper(II) ions are widely distributed in biological systems, a significant amount of research has centered on the search for relatively simple copper(II) complexes which may display some of the properties of the metalloproteins. One such system of potential importance is that formed by copper(II) halides with pyridine and substituted pyridines [3]. Small low-molecular-weight copper(II) coordination complexes with N-donor ligands have frequently been used to model the active site in copper proteins with the aim of obtaining insight into the correlation between structure and the spectroscopic and magnetic behavior [4–7].

Cobalt(II) complexes are important in biology mainly because of coenzyme B_{12} [8]. 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 [9–16]. Electronic properties of cobalt(II) compounds have received substantial attention [17–19] in part due to the fact that many of these complexes bind oxygen reversibly [20] 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 [21]. Cobalt ethylenediamine complexes are potent anti-microbial agents [22]. Low-spin cobalt porphyrins [23, 24] are of interest since cobalt-substituted hemoglobin, “coboglobin”, binds oxygen in a cooperative fashion [25]. The growth of cobalt 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 [26]. Strong magnetic anisotropy of high-spin cobalt(II) is at the origin of the increasing interest in polynuclear compounds containing this metal ion [27]. Several examples of high-nuclear complexes with six-coordinate cobalt(II) behaving as single molecule magnets and single chain magnets have been reported [28–31]. We have been interested in copper(II) and

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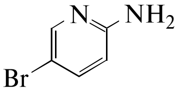
cobalt(II) complexes with 2-amino-5-bromopyridine as ligand (**L**)



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 (FT-IR), electronic spectra, room temperature magnetic moments, and a crystal structure.

EXPERIMENTAL

All of the chemicals and solvents were purchased from Merck Chemical Company and used as received without further purification.

Synthesis of $[Cu(L)_2(Cl)_2]$ (I). One mmol of copper(II) chloride dehydrates and 2.1 mmol of 2-amino-5-bromopyridine were each dissolved in 25 mL of CH_3OH. The Cu(II) salt solution was then added slowly to the ligand solution, thereby preventing any precipitation. The solution was filtered to remove any solids. After the solution stood for 5 days, the product was separated. The yield was about 85%.

For $C_{10}H_{10}N_4Cl_2Br_2Cu$ (**I**)				
anal. calcd., %:	C, 25.00;	H, 2.10;	N, 11.66;	Cu, 13.26.
Found, %:	C, 24.89;	H, 2.21;	N, 11.43;	Cu, 13.68.

Synthesis of $[Co(L)_2(Cl)_2]$ (II). One mmol of cobalt(II) chloride dehydrates and 2.1 mmol of 2-amino-5-bromopyridine were each dissolved in 25 mL of CH_3OH. The Co(II) salt solution was then added slowly to the ligand solution, thereby preventing any precipitation. The solution was filtered to remove any solids. After the solution stood for 5 days, the product was separated. The yield was about 79%.

For $C_{10}H_{10}N_4Cl_2Br_2Co$ (**II**)				
anal. calcd., %:	C, 25.24;	H, 2.12;	N, 11.77;	Co, 12.38.
Found, %:	C, 25.57;	H, 2.17;	N, 11.96;	Co, 12.62.

Physical measurements. C, H, and N determination were undertaken using an Elementar Analysis System GmbH Vario EL II. Copper and cobalt were determined on a PerkinElmer 2380 Atomic Absorption Spectrophotometer. Electronic spectra were recorded on a PerkinElmer Lambda 900 spectrophotometer using the diffuse reflectance technique, and MgO was used as a reference. FT-IR spectra were obtained in the 4000–300 cm^{-1} range as KBr disks by using a Galaxy series FTIR 5000 spectrophotometer. The spectra were calibrated using the polystyrene bands at 3028, 1601, and 1208 cm^{-1}. X-Band electron paramagnetic resonance spectra were recorded of both powdered and frozen solutions of the complexes at both room temperature and at liquid nitrogen temperature in DMF or in DMSO on an IBM electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. The room temperature magnetic moment of each complex was measured according to the Evans method. H NMR determination was carried out on a Bruker 300 MHz spectrometer.

X-ray structure determination. The X-ray measurement of **I** was made on a Bruker–Nonius X8 Apex II diffractometer equipped with a CCD area detector by sung graphite-monochromated MoK_α radiation (λ = 0.71073 Å) generated from a sealed tube source. Data were collected and reduced by SAINT software in the Bruker package [32]. The structure was solved by direct methods [33] and then developed by least squares refinement on F^2 [34, 35]. OLEX2 program for Windows was used to draw the structure [36]. All non-H atoms were placed in calculated positions and refined as isotopic with the "riding-model technique." The complete conditions of the data collection and structure are given in Table 1. Selected bond lengths and bond angles are presented in Table 2. Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 860012; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The spectroscopic data for both compounds are presented in Table 3. The electronic spectra of the complexes were obtained from a solid sample using the diffuse reflectance technique. Compound **I** shows a broad band at about 720 nm. This band represents the ligand field transition for the CuN_2Cl_2 chromophore [37, 38]. The second absorption bands at 270 nm are assigned to charge transfer from the non-bonding orbital of chloride ions to the vacant copper(II) *d* orbitals [37, 39]. The last absorption band observed at about 257 nm is associated with $\pi \to \pi^*$ or $n \to \pi^*$ transitions of the ligand [40]. On the basis of simplest model three spin-allowed bands are expected in tetrahedral cobalt(II) complexes, i.e., ${}^4A_2(F) \to {}^4T_2(F)$, ${}^4A_2(F) \to {}^4T_1(F)$ and ${}^4A_2(F) \to {}^4T_1(P)$. Usually such complexes show two bands between 830 and 625 nm, which can be assigned to ${}^4A_2(F) \to {}^4T_2(F)$ and ${}^4A_2(F) \to {}^4T_1(F)$, respectively; ${}^4A_2(F) \to {}^4T_1(P)$ is usually observed as a well-defined shoulder at about 550 nm [41]. The UV-Vis spectra of complex **II** were obtained from solid sample using diffuse reflectance technique. The compound shows a broad shoulder with bands at 810, 640, and 535 nm, corresponding to $d \to d$ transitions. Absorption at 290 nm is assigned to charge transfer from the non-bonding orbital of chloride ions to half-filled *d* orbitals of cobalt(II) [42]. Absorption at 259 nm is

Table 1. Crystal data and refinement parameters for structure **I**

Parameter	Value
Formula weight	480.48
T, K	296(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	12.8921(4)
b, Å	4.22090(10)
c, Å	15.6291(4)
β, deg	113.730(2)
V, Å^3	778.57(4)
Z	2
ρ_{calcd}, mg/m^3	2.050
Absorption coefficient, mm^{-1}	6.868
F(000)	462
Crystal size, mm	0.54 × 0.09 × 0.04
θ Range for data collection, deg	3.45–28.11
Limiting indices	$-17 \le h \le 17$, $-5 \le k \le 5$, $-20 \le l \le 20$
Reflections collected/unique (R_{int})	23239/1902 (0.0388)
Completeness to θ = 28.11, %	99.7
Refinement method	Full-matrix least-squares on F^2
Parameters	88
Goodness-of-fit on F^2	0.985
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0329$, $wR_2 = 0.0943$
R indices (all data)	$R_1 = 0.0451$, $wR_2 = 0.1026$
Largest diff. peak and hole, e Å^{-3}	1.210 and –0.866

$w = 1/[\delta^2(F_o^2) + (0.0613P)^2 + 0.7908P]$. $P = (F_o^2 + 2F_c^2)/3$.
$S = \Sigma[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg) of structure **I**

Bond	d, Å	Angle	ω, deg
Br–C(1)	1.884(3)	C(5)N(2)C(4)	118.4(3)
Cl–Cu	2.2584(7)	C(5)N(2)C(4)	118.4(3)
N(2)–C(5)	1.348(4)	C(4)N(2)Cu	126.8(2)
N(2)–C(4)	1.350(4)	C(5)C(1)C(2)	119.6(3)
N(2)–Cu	2.039(2)	C(5)C(1)Br	119.1(3)
C(1)–C(5)	1.355(4)	C(2)C(1)Br	121.3(3)
C(1)–C(2)	1.389(5)	C(3)C(2)C(1)	118.3(3)
C(2)–C(3)	1.348(5)	C(2)C(3)C(4)	120.8(3)
C(2)–H(2)	0.9300	N(1)C(4)N(2)	119.2(3)
C(3)–C(4)	1.407(4)	N(1)C(4)C(3)	120.7(3)
C(3)–H(3)	0.9300	N(2)C(4)C(3)	120.1(3)
C(4)–N(1)	1.334(4)	N(2)C(5)C(1)	122.8(3)
Cu–N(2)	2.039(2)	N(2)CuCl	88.66(7)

associated with π → π* or n → π* transitions of the ligand [43, 44].

The IR spectra of the free ligand and the complexes were obtained in the range of 4000–300 cm^{-1}. All the bands present in the IR spectra of the free ligand were also observed in the spectra of the complexes. Based on data from earlier reports, we assigned bands at 459 and 434 cm^{-1} for **I** and **II**, respectively, to M–N vibrations. M–Cl vibrations for **I** and **II** are assigned to 334 and 322 cm^{-1}, respectively [45–48].

The magnetic moment of both complexes were determined by the Evans method [49]. 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. The shift of a proton resonance line of an inert substance due to the presence of paramagnetic ions is given by theoretical expression:

$$\Delta v/v_0 = (2\pi/3)(\chi_v - \chi_{v'}). \quad (1)$$

In this equation Δv is the shift, v_0 is the applied field, χ_v is the volume susceptibility of the solution containing paramagnetic ions and $\chi_{v'}$ is the volume susceptibility of the reference solution. The values of 1.78 and 4.12 were found for complexes **I** and **II**, respectively.

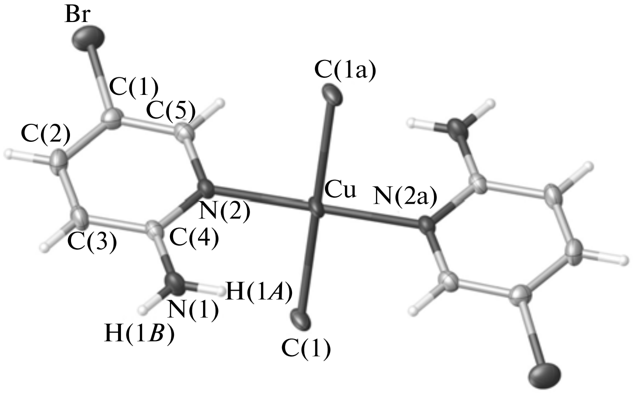
The electron spin resonance (ESR) spectra of complex **I** in powder and in frozen solution form were recorded at X-band frequencies at room temperature and at liquid nitrogen temperature to aid in determining the ground-state configuration of copper(II) ions. In the solid state, the spectra shows only a weak and broad signal ($g_{aver} = 2.15$). Such behavior is also found in [50]. The observed frozen solution (77 K) ESR spectra of the compound in DMSO or DMF shows two bands located at $g_{\parallel} = 2.32$ and $g_{\perp} = 2.07$ corresponding to the $\Delta M_S = \pm 1$ transition. This feature is typical for copper(II) complexes. The $g_{\parallel} > g_{\perp} > 2.0023$, also exhibit large parallel hyperfine splitting and are associated with the $d_{x^2-y^2}$ ground state [51]. In the spectrum of complex **I**, the parallel region is clearly resolved and all four transitions derived from the Cu ($I = 3/2$) hyperfine splitting can be directly observed. These hy-

Table 3. Spectroscopic data for complexes **I** and **II**

Complex	IR (Cu–N), (Cu–Cl), (Co–N), (Co–Cl), cm^{-1}	UV-Vis, nm	ESR (powder) complex **I**	ESR (in DMSO or DMF) complex **I**	μ (R.T.), μ_B
I	459	720	2.15	$g_{\parallel} = 2.32$	
	334	270		$g_{\perp} = 2.07$	1.78
		257		$A_{\parallel} = 160 \times 10^4$	
				$A_{N\perp} = 14 \times 10^4$	
II	434	810, 640			4.12
	322	535, 290			
		259			

perfine lines for complexes split the $g_{\parallel}$ signal with an average spacing of 160×10^{-4} cm^{-1}. In the perpendicular region, the spectrum is not well resolved, although some superhyperfine structure is observed. The lack of clear resolution in this spectral region is presumably due to the large number of overlapping $\Delta M_I = 0$ and $\Delta M_I > 0$ transitions and to the large intrinsic widths of the individual transitions. The structure observed in the perpendicular region of the spectra is due to nitrogen superhyperfine splitting of the ligands. The $A_{N\perp}$ value of $\approx 14 \times 10^{-4}$ cm^{-1} and the presence of three weak resolved peaks for the nitrogen superhyperfine structure of the complex are in accordance with expectations for two N donors per copper(II) ions [52].

The solid state structure of complex **I** determined by single-crystal X-ray diffraction, together with atom labeling is shown in figure. The structure of complex **I** consists of a Cu surrounded by two ligands and two chlorides. In this complex, Cu(II) has a slightly distorted square planar geometry with trans position of two halides. The structure is essentially a D_{2h} symmetric and the copper(II) ion is four coordinate, as expected with *trans* halides. The Cu–N distances are 2.039 Å and Cu–Cl 2.2584 Å. The angles NCuN and ClCuCl are 180°, while the N(2a)CuCla and N(2)CuCl angles are 88.66°. The angles N(2)CuCla and N(2a)CuCl are 91.34°. Four-coordinate copper(II) compounds with two different ligands are almost distorted square planar symmetry from a coupling between electronic and vibration wave factions that lower the ground-state energy [53].



Crystal structure of complex **I**.

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REFERENCES

1. Kokoszoka, G.E. and Duerset, R.W., *Coord. Chem. Rev.*, 1970, vol. 5, p. 209.
2. Hoffmann, R., Hay, P.J., and Thibeault, J.C., *J. Am. Chem. Soc.*, 1975, vol. 97, p. 4884.
3. Reedijk, J., in: Comprehensive Coordination Chemistry, Wilkinson G., Ed., Oxford: Pergamon, 1987.
4. Collinson, S.R. and Fenton, D.E., *Coord. Chem. Rev.*, 1996, vol. 148, p. 19.
5. Mandal, S., Das, G., and Singh, R., *Coord. Chem. Rev.*, 1997, vol. 160, p. 191.
6. Kaim, W. and Rall, J., *Angew. Chem. Int. Engl.*, 1996, vol. 35, p. 43.
7. Estes, W.E., Andrews, C.W., Wasson, J.R., and Hatfield, W.E., *Inorg. Chem.*, 1972, vol. 11, p. 1657.
8. Yang, L., Crans, D.C., Miller, S.M., et al., *Inorg. Chem.*, 2002, vol. 41, p. 4859.
9. Sakar, F., Ybarra, J., Leahy, P., et al., *Am. J. Physiol.*, 1998, vol. 274, p. E984.
10. Ybarra, J., Behrooz, A., Gabriel, A., et al., *Mol. Cell. Endocrinol.*, 1997, vol. 133, p. 151.
11. Yuen, V.A., Orvig, C., and McNeill, J.H., *Can. J. Physiol. Pharmacol.*, 1993, vol. 71, p. 263.
12. Fugono, J., Yasui, H., and Sakurai, H., *J. Pharm. Pharmacol.*, 2010, vol. 53, p. 1247.
13. Cohen, N., Halberstam, M., Shlimovich P., et al., *J. Clin. Invest.*, 1995, vol. 95, p. 2501.
14. Golfine, A.B., Patti, M.E., Zuberi, L., et al., *Metab. Clin. Exp.*, 2000, vol. 49, p. 400.
15. Crans, D.C., *J. Inorg. Biochem.*, 2000, vol. 30, p. 123.

16. Crans, D.C., Yang, L., Jakusch, T., and Kiss, T., *Inorg. Chem.*, 2000, vol. 39, p. 4409.
17. Stevens, J.C. and Bush, D.H., *J. Am. Chem. Soc.*, 1980, vol. 102, p. 3283.
18. Gok, Y., *Polyhedron*, 1994, vol. 13, p. 1793.
19. Lance, K.A., Goldsby, K.A., and Bush, D.H., *Inorg. Chem.*, 1990, vol. 29, p. 4537.
20. Srivanavit, C. and Brown, D.G., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 4447.
21. Kumaragura, N., Sathakumar, S., and Arunugham, M.N., *Polyhedron*, 2006, vol. 25, p. 3253.
22. Nagababu, P., Latha, J., Navveena, L., et al., *Can. J. Microbiol.*, 2006, vol. 52, p. 1247.
23. Zharnikova, M.A., Balakirev, A.E., Maizlish, V.E., and Shaposhnikov, G.P., *Russ. J. Gen. Chem.*, 2002, vol. 72, p. 131.
24. Balakirev, A.E., Maizlish, V.E., Balakireva, O.V., et al., *Russ. J. Gen. Chem.*, 2004, vol. 74, p. 295.
25. Haffman, B.M. and Petering, D.H., *Proc. Natl. Acad. Sci.*, 1970, vol. 67, p. 637.
26. Kurmoo, M., *Chem. Soc. Rev.*, 2009, vol. 38, p. 353.
27. Lloret, F., Julve, M., Cano, J., et al., *Inorg. Chem.*, 2008, vol. 361, p. 3432.
28. Langley, S., Heliwell, M., Sessoli, R., et al., *Inorg. Chem.*, 2008, vol. 47, p. 497.
29. Ferguson, A., Parkin, J., Sabchez-Benitz, J., et al., *Chem. Commun.*, 2007, p. 3473.
30. Miyasaka, H., Julve, M., Yamashita, M., and Clerac, R., *Inorg. Chem.*, 2009, vol. 48, p. 3420.
31. Pardo, E., Ruiz-Garcia, R., Lloret, F., et al., *Chem. Eur. J.*, 2007, vol. 13, p. 2054.
32. *SAINT, Version 6.02*, Madison (WI, USA): Bruker AXS Inc., 1999.
33. Burla, M.C., Caliandro, R., Camalli, M., et al., *J. Appl. Crystallogr.*, 2005, vol. 38, p. 381.
34. Sheldrick, G.M., *SHELXL-97*, *Program for Crystal Structure Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.
35. *SHELXT L.N., Version 5.10*, Madison (WI, USA): Bruker Analytical X-Ray Inc., 1998.
36. Farrugia, L.J., *J. Appl. Crystalloger.*, 1997, vol. 30, p. 566.
37. Berreau, L.M., Young, V.G., Jr., and Woo, L.K., *Inorg. Chem.*, 1985, vol. 34, p. 3485.
38. Lever, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1984.
39. Justin Thomas, K.R., Tharmaraj, P., Chandrasekhar, V., et al., *Polyhedron*, 1995, vol. 14, p. 977.
40. Bailey, N.A., Fenton D.A., Moody R., et al., *Dalton Trans.,* 1987, p. 2519.
41. Kurzak, K., Plunere, P., Lehn, J.M., et al., *J. Am. Chem. Soc.*, 1982, vol. 104, p. 6330.
42. Hasanvand, F., Hiseinzadeh, A., Zolgharnein, J., and Amani, S., *J. Coord. Chem.*, 2010, vol. 63, p. 346.
43. Amani, S., Van Albada, G.A., and Reedijk, J., *Transition Met. Chem.*, 1999, vol. 24, p. 104.
44. Rodrigues, L., Labisbal, E., Sousa-Pedrares, A., et al., *Inorg. Chem.*, 2006, vol. 45, p. 7903.
45. Drew, G.B. and Yates, P.C., *Dalton Trans.*, 1988, p. 2995.
46. Mabbs, F.E., *Chem. Soc. Rev.*, 1993, vol. 22, p. 313.
47. Weder, J.E., Hambley, T.W., Kennedy, B.J., et al., *Inorg. Chem.*, 1999, vol. 38, p. 1736.
48. Stankowski, J., *J. Mol. Struc.*, 2001, vol. 597, p. 109.
49. Evans, D.F., *J. Chem. Soc.*, 1959, p. 2003.
50. Hasanvand, F., Nasrollahi, N., Vajed, A., and Amani, S., *Malay. J. Chem.*, 2010, vol. 12, p. 27.
51. Manzur, J., Mora, H., Vega, A., et al., *Inorg. Chem.,* 2007, vol. 6, p. 6924.
52. Kovala-Demertzi, D., Skrzypek, D., Szymanska, B., et al., *Inorg. Chim. Acta*, 2005, vol. 358, p. 186.
53. Fu, Z. and Chivers, T., *Can. J. Chem.*, 2006, vol. 84, p. 140.