

Research Article

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

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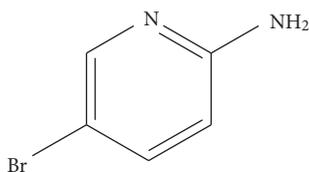
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The synthesis, spectroscopic, and magnetic characterization of two new copper(II) and cobalt(II) complexes are described. Both two compounds have the general formula $[M(L)_2(Cl)_2]$, in which $L = 2$ -amino-5-bromopyridine. These complexes were prepared in one-step synthesis and characterized by elemental analysis, FTIR, UV-Vis, and EPR spectroscopy. Moreover, the single crystal structure of complex (1) 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 \rightarrow metal charge transfer, and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand. The FTIR spectra show MN_2Cl_2 vibrations at $500-300\text{ cm}^{-1}$. The complexes show room temperature magnetic moments of 1.78 BM and 4.12 BM 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.

1. 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 B₁₂ [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 B₁₂. Cobalt is a necessary trace element in mammals and has many uses in



SCHEME 1: Structure of ligand.

medicine, magnetic resonance imaging, and drug delivery [21]. Cobalt ethylenediamine complexes are potent antimicrobial 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 magnetochemistry, 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 cobalt(II) complexes with 2-amino-5-bromopyridine as ligand. 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 of the chemicals and solvents were purchased from Merck Chemical Company and used as received without further purification.

2.2. Preparation of the Complexes. The coordination compounds were prepared according to the general procedure (Scheme 1) [17].

Complex [Cu(2-amino-5-bromopyridine)₂(Cl)₂]; (1). One mmol of copper(II) chloride hydrates and 2.1 mmol of 2-amino-5-bromopyridine (Scheme 1) were each dissolved in 25 mL of CH₃OH. The Cu(II) salt solution was then added slowly to the ligand solution, thereby preventing any precipitation, and the solution was filtered to remove any solids. After the solution stood for five days, the product was separated. Yield about 85%.

Elemental analysis for CuC₁₀H₁₀N₄Br₂Cl₂; (1); found: C, 24.89; H, 2.21; N, 11.43; Cu, 13.68%. Cal.; C, 25.00; H, 2.10; N, 11.66; Cu, 13.26%.

Complex [Co(2-amino-5-bromopyridine)₂(Cl)₂]; (2). One mmol of cobalt(II) chloride hydrates and 2.1 mmol of 2-amino-5-bromopyridine each dissolved in 25 mL of CH₃OH. The Co(II) salt solution was then added slowly to the

TABLE 1: Crystal data and refinement parameters for [Cu(2-amino-5-bromopyridine)₂(Cl)₂].

Empirical formula	C ₁₀ H ₁₀ Br ₂ Cl ₂ CuN ₄
Formula weight	480.48
T (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 (1)/n
a (Å)	12.8921(4)
b (Å)	4.22090(10)
c (Å)	15.6291(4)
α (°)	90
β (°)	113.730(2)
γ (°)	90
Vol. (Å ³)	778.57(4)
Z	2
Calculated density (Mg/m ³)	2.050
Absorption coefficient (mm ⁻¹)	6.868
F(000)	462
Crystal size (mm)	0.54 × 0.09 × 0.04
Theta range for data collection (°)	3.45 to 28.11
	-17 ≤ h ≤ 17
Limiting indices	-5 ≤ k ≤ 5
	-20 ≤ l ≤ 20
Reflections collected/unique	23239/1902 [R(int) = 0.0388]
Completeness to theta	28.11, 99.7%
Refinement method	Full-matrix least squares on F ²
Data/restraints/parameters	1902/0/88
Goodness-of-fit on F ²	0.985
Final R indices [I > 2σ(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

$$W = 1/[\delta^2(F_o^2) + (0.0613P)^2 + 0.7908P].$$

$$P = (F_o^2 + 2 F_C^2)/3.$$

$$S = \sum [w(F_o^2 - F_C^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}.$$

ligand solution, thereby preventing any precipitation, and the solution was filtered to remove any solids. After the solution stood for five days, the product was separated. Yield about 79%.

Elemental analysis for CoC₁₀H₁₀N₄Br₂Cl₂; (2); found: C, 25.57; H, 2.17; N, 11.96; Co, 12.62%. Cal.; C, 25.24; H, 2.12; N, 11.77; Co, 12.38%.

3. 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 Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. Electronic spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, and MgO was used as a reference. FTIR spectra were obtained in the 4000–300 cm⁻¹ range as KBr disks by using a Galaxy series

TABLE 2: Spectroscopic data for both complexes.

Complex	IR (Cu-N) cm^{-1} IR (Cu-Cl) cm^{-1} IR (Co-N) cm^{-1} IR (Co-Cl) cm^{-1}	UV-Vis (nm)	ESR (powder)	ESR (solution)	μ (R.T)
(1)	459 334	720 270 257	2.15	$g_{\parallel} = 2.32$ $g_{\perp} = 2.07$ $A_{\parallel} = 160 \times 10^{-4}$ $A_{N\perp} = 14 \times 10^{-4}$	1.78
(2)	434 322	810, 640 535, 290 259	—	—	4.12

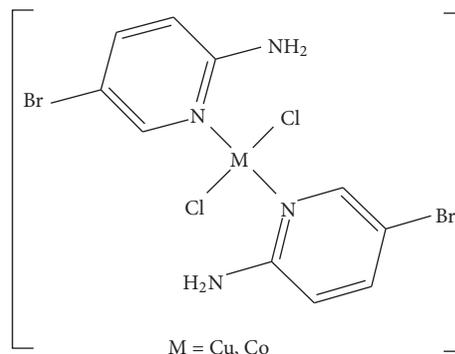
TABLE 3: Selected bond distances [\AA] and angles [$^{\circ}$].

Lengths [\AA]		Angles [$^{\circ}$]	
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(3)-C(2)-H(2)	120.9
C(2)-H(2)	0.9300	C(1)-C(2)-H(2)	120.9
C(3)-C(4)	1.407(4)	C(2)-C(3)-C(4)	120.8(3)
C(3)-H(3)	0.9300	C(2)-C(3)-H(3)	119.6
C(4)-N(1)	1.334(4)	C(2)-C(3)-H(3)	119.6
C(5)-H(5)	0.9300	N(1)-C(4)-N(2)	119.2(3)
N(1)-H(1A)	0.8600	N(1)-C(4)-C(3)	120.7(3)
N(1)-H(1B)	0.8600	N(2)-C(4)-C(3)	120.1(3)
Cu-N(2)a	2.039(2)	N(2)-C(5)-C(1)	122.8(3)
Cu-Cl(a)	2.2584(7)	N(2)-C(5)-H(5)	118.6
		C(1)-C(5)-H(5)	118.6
		C(1)-C(5)-H(5)	118.6
		C(4)-N(1)-H(1A)	120.0
		C(4)-N(1)-H(1B)	120.0
		H(1A)-N(1)-H(1B)	120.0
		N(2)a-Cu-N(2)	180.00(14)
		N(2)a-Cu-Cl(a)	88.66(7)
		N(2)-Cu-Cl(a)	91.34(7)
		N(2)a1-Cu-Cl	91.34(7)
		N(2)-Cu-Cl	88.66(7)

Symmetry transformations used to generate equivalent atoms:

#1 $-x, -y + 2, -z + 1$.

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



SCHEME 2: Structure of complexes.

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.

4. Crystal Structure Determination and Refinement

The X-ray measurement of complex (1) was made on a Bruker-Nonius X8 ApexII diffractometer equipped with a CCD area detector by sung graphite-monochromated Mo α radiation ($\lambda = 0.71073 \text{\AA}$) 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 isotropic with the "riding-model technique." The complete conditions of the data collection and structure are given in Table 1.

5. Results and Discussion

5.1. Electronic Spectra. The spectroscopic data for both compounds (Scheme 2) are presented in Table 2. The electronic spectra of the complexes were obtained from a solid sample using the diffuse reflectance technique. Copper(II) compound (1) shows a broadband 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 nonbonding 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 $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [40]. On the basis of simplest model three spin-allowed bands are expected in tetrahedral cobalt(II) complexes, that is, ${}^4A_2(\text{F}) \rightarrow {}^4T_2(\text{F})$, ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{F})$, and ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{P})$. Usually such complexes show two bands between 830 and 625 nm, which can be assigned to ${}^4A_2(\text{F}) \rightarrow {}^4T_2(\text{F})$ and ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{F})$, respectively; ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{P})$ is usually observed as a well-defined shoulder at about 550 nm [41]. The UV-Vis spectra of complex (2) were obtained from solid sample using diffuse reflectance technique. The compound shows a broad shoulder with bands at 810, 640, and 535 nm is due to $d \rightarrow d$ transitions. Absorption at 290 is assigned to charge transfer from the nonbonding orbital of chloride ions to half-filled d orbitals of cobalt(II) [42]. Absorption at 259 nm is associated with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [43, 44].

5.2. Infrared Spectra. The IR spectra of the free ligand and the complexes were obtained in the range of $4000\text{--}300\text{ cm}^{-1}$. 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 [45, 46], we assigned bands at 459 and 434 cm^{-1} for (1) and (2), respectively, to M-N vibrations. M-Cl vibrations for (1) and (2) are assigned to 334 and 322 cm^{-1} , respectively [47, 48].

5.3. Magnetic Moment. 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:

$$\frac{\Delta\nu}{\nu_0} = \left(\frac{2\pi}{3}\right)(\chi_v - \chi'_v). \quad (1)$$

In this equation $\Delta\nu$ is the shift, ν_0 is the applied field, χ_v is the volume susceptibility of the solution containing paramagnetic ions, and χ'_v is the volume susceptibility of the reference solution. The values of 1.78 and 4.12 were found for complexes (1) and (2), respectively.

5.4. Electron Spin Resonance. The electron spin resonance (ESR) spectra of complex (1) 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 ($g_{\text{ave.}} = 2.15$). Such behavior is also found in the literature [50]. The observed frozen solution (77 K) ESR spectra of the compound in DMSO or DMF shows two bands

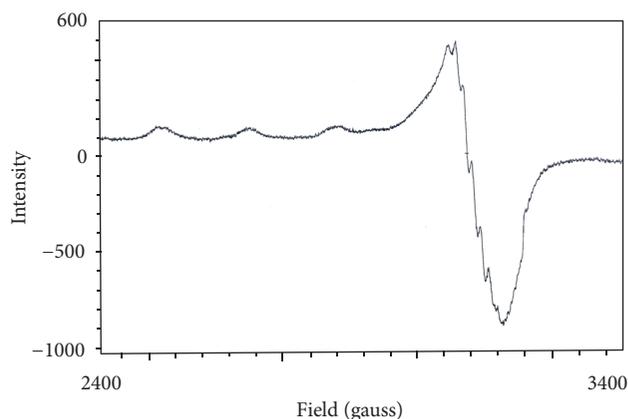


FIGURE 1: ESR spectra of Cu(II) complex in DMF at liquid nitrogen temperature.

located at $g_{\parallel} = 2.32$ and $g_{\perp} = 2.07$ corresponding to the $\Delta M_S = \pm 1$ transition. This feature (Figure 1) 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, the parallel region is clearly resolved, and all four transitions derived from the Cu ($I = 3/2$) hyperfine splitting can be directly observed. These hyperfine lines for complexes split the g_{\parallel} signal with an average spacing of $160 \times 10^{-4}\text{ cm}^{-1}$. 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 $\approx 14 \times 10^{-4}\text{ cm}^{-1}$ and the presence of three peaks for the nitrogen superhyperfine structure of the complex are in accordance with expectations for two N donors per copper(II) ions [52, 53].

6. Description of the Crystal Structure of Complex (1)

The solid-state structure of complex (1) determined by single-crystal X-ray diffraction, together with atom labeling is shown in Figure 2. Selected bond lengths and bond angles are presented in Table 3. Crystallographic data and structure.

Refinement parameters are summarized in Table 1. The structure of complex (1) 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 \AA and Cu-Cl 2.2584 \AA . The angles N-Cu-N and Cl-Cu-Cl are 180.0° , while the N(2)a-Cu-Cl(a) and N(2)-Cu-Cl angles are 88.66° . The angles N(2)-Cu-Cl(a) and N(2)a-Cu-Cl are 91.34° . Four-coordinate copper(II) compounds with two

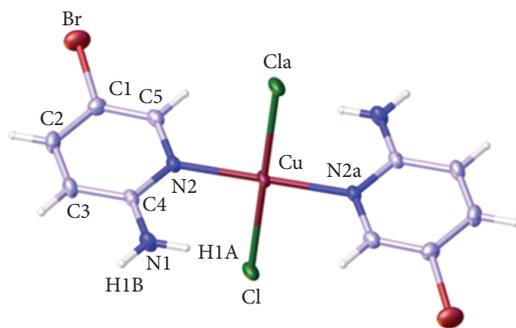


FIGURE 2: Crystal structure of complex $[\text{Cu}(\text{2-amino-5-bromopyridine})_2(\text{Cl})_2]$.

different ligands are almost distorted square planar symmetry from a coupling between electronic and vibration wave functions that lower the ground-state energy [54].

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References

- [1] G. F. Kokoszka and R. W. Duerst, "Epr studies of exchange coupled metal ions," *Coordination Chemistry Reviews*, vol. 5, no. 2, pp. 209–244, 1970.
- [2] P. J. Hay, J. C. Thibeault, and R. Hoffmann, "Orbital interactions in metal dimer complexes," *Journal of the American Chemical Society*, vol. 97, no. 17, pp. 4884–4899, 1975.
- [3] J. Reedijk, "Heterocyclic nitrogen-donor ligands," in *Comprehensive Coordination Chemistry*, G. Wilkinson, Ed., vol. 2, pp. 73–98, Pergamon, Oxford, UK, 1987.
- [4] S. R. Collinson and D. E. Fenton, "Metal complexes of bibrachial Schiff base macrocycles," *Coordination Chemistry Reviews*, vol. 148, pp. 19–40, 1996.
- [5] S. Mandal, G. Das, R. Singh, R. Shukla, and P. K. Bharadwaj, "Synthesis and studies of Cu(II)-thiolato complexes: bioinorganic perspectives," *Coordination Chemistry Reviews*, vol. 160, pp. 191–235, 1997.
- [6] W. Kaim, J. Rall, and J. Rall, "Copper a "modern" bioelement," *Angewandte Chemie*, vol. 35, no. 1, pp. 43–60, 1996.
- [7] P. Singh, D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, "Out-of-plane interactions in parallel-planar copper(II) dimers. The structure and magnetic properties of dibromobis(2-methylpyridine)copper(II)," *Inorganic Chemistry*, vol. 11, no. 7, pp. 1657–1661, 1972.
- [8] L. Yang, D. C. Crans, S. M. Miller et al., "Cobalt(II) and cobalt(III) dipicolinate complexes: solid state, solution, and in vivo insulin-like properties," *Inorganic Chemistry*, vol. 41, no. 19, pp. 4859–4871, 2002.
- [9] F. Saker, J. Ybarra, P. Leahy, R. W. Hanson, S. C. Kalhan, and F. Ismail-Beigi, "Glycemia-lowering effect of cobalt chloride in the diabetic rat: role of decreased gluconeogenesis," *American Journal of Physiology*, vol. 274, no. 6, pp. E984–E991, 1998.
- [10] J. Ybarra, A. Behrooz, A. Gabriel, M. H. Koseoglu, and F. Ismail-Beigi, "Glycemia-lowering effect of cobalt chloride in the diabetic rat: increased GLUT1 mRNA expression," *Molecular and Cellular Endocrinology*, vol. 133, no. 2, pp. 151–160, 1997.
- [11] V. G. Yuen, C. Orvig, and J. H. McNeill, "Glucose-lowering effects of a new organic vanadium complex, bis(maltolato)oxovanadium(IV)," *Canadian Journal of Physiology and Pharmacology*, vol. 71, no. 3-4, pp. 263–269, 1993.
- [12] J. Fugono, H. Yasui, and H. Sakurai, "Pharmacokinetic study on gastrointestinal absorption of insulinomimetic vanadyl complexes in rats by ESR spectroscopy," *Journal of Pharmacy and Pharmacology*, vol. 53, no. 9, pp. 1247–1255, 2001.
- [13] N. Cohen, M. Halberstam, P. Shlimovich, C. J. Chang, H. Shamon, and L. Rossetti, "Oral vanadyl sulfate improves hepatic and peripheral insulin sensitivity in patients with non-insulin-dependent diabetes mellitus," *Journal of Clinical Investigation*, vol. 95, no. 6, pp. 2501–2509, 1995.
- [14] A. B. Golfine, M. E. Patti, L. Zuberi et al., "Excess weight gain and obesity science and research," *Metabolism Clinical and Experimental*, vol. 49, pp. 400–410, 2000.
- [15] D. C. Crans, "Chemistry and insulin-like properties of vanadium(IV) and vanadium(V) compounds," *Journal of Inorganic Biochemistry*, vol. 80, no. 1-2, pp. 123–131, 2000.
- [16] D. C. Crans, L. Yang, T. Jakusch, and T. Kiss, "Aqueous chemistry of ammonium (dipicolinato)oxovanadate(V): the first organic vanadium(V) insulin-mimetic compound," *Inorganic Chemistry*, vol. 39, no. 20, pp. 4409–4416, 2000.
- [17] J. C. Stevens, P. J. Jackson, W. P. Schammel, G. G. Christoph, and D. H. Busch, "Synthesis and structure of totally synthetic coboglobin models," *Journal of the American Chemical Society*, vol. 102, no. 9, pp. 3283–3285, 1980.
- [18] Y. Gok, "Synthesis and characterization of new (E,E)-dioximes and their cobalt(III) complexes containing crown ether moieties," *Polyhedron*, vol. 13, no. 11, pp. 1793–1800, 1994.
- [19] K. A. Lance, K. A. Goldsby, and D. H. Busch, "Effective new cobalt(II) dioxygen carriers derived from dimethylglyoxime by the replacement of the linking protons with BF_2^+ ," *Inorganic Chemistry*, vol. 29, no. 22, pp. 4537–4544, 1990.
- [20] C. Srivanavit and D. G. Brown, "Isotropic proton shifts for Co(salen)," *Journal of the American Chemical Society*, vol. 98, no. 15, pp. 4447–4449, 1976.
- [21] N. Kumaraguru, K. Santhakumar, S. Arunachalam, and M. N. Arumugham, "Synthesis, characterization and micellization behaviour of some surface active mixed-ligand complexes of cobalt(III)," *Polyhedron*, vol. 25, no. 17, pp. 3253–3260, 2006.
- [22] P. Nagababu, J. Naveena Lavanya Latha, P. Pallavi, S. Harish, and S. Satyanarayana, "Studies on antimicrobial activity of cobalt(III) ethylenediamine complexes," *Canadian Journal of Microbiology*, vol. 52, no. 12, pp. 1247–1254, 2006.
- [23] M. A. Zharnikova, A. E. Balakirev, V. E. Maizlish, and G. P. Shaposhnikov, "Cobalt(II) tetraaminotetranitrophthalocyanine and its N-acyl derivatives," *Russian Journal of General Chemistry*, vol. 72, no. 1, pp. 131–132, 2002.
- [24] A. E. Balakirev, V. E. Maizlish, O. V. Balakireva, G. P. Shaposhnikov, V. V. Bykova, and N. V. Usoltseva, "Metal phthalocyanines with undecyloxybenzoic acid residues, and their mesomorphic properties," *Russian Journal of General Chemistry*, vol. 74, no. 2, pp. 295–299, 2004.

- [25] B. M. Hoffman and D. H. Petering, "Coboglobins: oxygen-carrying cobalt-reconstituted hemoglobin and myoglobin," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 67, no. 2, pp. 637–643, 1970.
- [26] M. Kurmoo, "Magnetic metal-organic frameworks," *Chemical Society Reviews*, vol. 38, no. 5, pp. 1353–1379, 2009.
- [27] F. Lloret, M. Julve, J. Cano, R. Ruiz-Garcia, and E. Pardo, "Syntheses and structures of three complexes of formulas $[L_3Co(\mu_2-O_2P(Bn)_2)_3CoL'] [L'']$, featuring octahedral and tetrahedral cobalt(II) geometries; variable-temperature magnetic susceptibility measurement and analysis on $[(py)_3Co(\mu_2-O_2P(Bn)_2)_3Co(py)] [ClO_4]$," *Inorganic Chemistry*, vol. 361, pp. 3432–3445, 2008.
- [28] S. Langley, M. Helliwell, R. Sessoli, S. J. Teat, and R. E. Winpenny, "Synthesis and structural and magnetic characterization of cobalt(II) phosphonate cage compounds," *Inorganic Chemistry*, vol. 47, no. 2, pp. 497–507, 2008.
- [29] A. Ferguson, A. Parkin, J. Sanchez-Benitez, K. Kamenev, W. Wernsdorfer, and M. Murrie, "A mixed-valence Co_7 single-molecule magnet with C_3 symmetry," *Chemical Communications*, no. 33, pp. 3473–3475, 2007.
- [30] H. Miyasaka, M. Julve, M. Yamashita, and R. Clérac, "Slow dynamics of the magnetization in one-dimensional coordination polymers: single-chain magnets," *Inorganic Chemistry*, vol. 48, no. 8, pp. 3420–3437, 2009.
- [31] E. Pardo, R. Ruiz-García, F. Lloret et al., "Ligand design for heterobimetallic single-chain magnets: synthesis, crystal structures, and magnetic properties of $MICuII$ ($M = Mn, Co$) chains with sterically hindered methyl-substituted phenyloxamate bridging ligands," *Chemistry: A European Journal*, vol. 13, no. 7, pp. 2054–2066, 2007.
- [32] Bruker AXS Inc., *SAINT (Version 6.02)*, Madison, Wisc, USA, 1999.
- [33] M. C. Burla, R. Caliendo, M. Camalli et al., "2-amino-3-methyl-6-[methyl(phenyl)amino]-5-nitropyrimidin-4(3H)-one: polarized molecules within hydrogen-bonded sheets," *Journal of Applied Crystallography*, vol. 38, pp. 381–388, 2005.
- [34] G. M. Sheldrick, *SHELXL97, Program For Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.
- [35] *SHELXT LN, Version 5.10*, Bruker Analytical X-ray, Madison, Wisc, USA, 1998.
- [36] L. J. Farrugia, "ORTEP-3 for windows—a version of ORTEP-III with a graphical user interface (GUI)," *Journal of Applied Crystallography*, vol. 30, no. 5, p. 565, 1997.
- [37] L. M. Berreau, V. G. Young, and L. K. Woo, "Synthesis, characterization, and reactivity of sulfido- and selenidomolybdenum(IV) porphyrin complexes. X-ray structure of sulfido(5,10,15,20-tetratolylporphyrinato)molybdenum(IV)," *Inorganic Chemistry*, vol. 34, no. 13, pp. 3485–3490, 1995.
- [38] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, The Netherlands, 2nd edition, 1984.
- [39] K. R. J. Thomas, P. Tharmaraj, V. Chandrasekhar, S. R. Scott, and A. Wallace Cordes, "Five-coordinate copper(II) complexes of $GEM-N_3P_3Ph_2(dmpz)_4$," *Polyhedron*, vol. 14, no. 8, pp. 977–982, 1995.
- [40] N. A. Bailey, D. E. Fenton, R. Moody et al., "Complexes of ligands providing endogenous bridges. Part 4. Copper(II) complexes of macrocyclic Schiff bases derived from 2,6-diacetylpyridine and 1,*n*-diamino-*n*'-hydroxyalkanes ($n, n' = 3, 2; 4, 2; \text{ and } 5, 3$): synthesis, properties, and structures," *Journal of the Chemical Society, Dalton Transactions*, no. 11, pp. 2519–2529, 1987.
- [41] J. Comarmond, P. Plumeré, J. M. Lehn et al., "Dinuclear copper(II) cryptates of macrocyclic ligands: synthesis, crystal structure, and magnetic properties. Mechanism of the exchange interaction through bridging azido ligands," *Journal of the American Chemical Society*, vol. 104, no. 23, pp. 6330–6340, 1982.
- [42] F. Hasanvand, A. Hoseinzadeh, J. Zolgharnein, and S. Amani, "Synthesis and characterization of two acetato-bridged dinuclear copper(II) complexes with 4-bromo-2-((4 or 6-methylpyridin-2-ylimino)methyl)phenol as ligand," *Journal of Coordination Chemistry*, vol. 63, no. 2, pp. 346–352, 2010.
- [43] S. A. Komaei, G. A. Van Albada, and J. Reedijk, "Synthesis, spectroscopic and magnetic properties of methoxo-bridged copper(II) complexes with 2-amino-4-methylpyridine as the ligand," *Transition Metal Chemistry*, vol. 24, no. 1, pp. 104–107, 1999.
- [44] L. Rodríguez, E. Labisbal, A. Sousa-Pedrares et al., "Coordination chemistry of amine bis(phenolate) cobalt(II), nickel(II), and copper(II) complexes," *Inorganic Chemistry*, vol. 45, no. 19, pp. 7903–7914, 2006.
- [45] M. G. B. Drew, P. C. Yates, F. S. Esho et al., "Dicopper(II) complexes of a binucleating N_4 macrocycle containing mono- and di-atomic bridges; Magnetic interactions mediated by alkoxo- and diaza-bridging ligands. Crystal structures of $[Cu_2(L^1)(pz)_2][ClO_4]_2$, $[Cu_2(L^1)(OEt)_2(NCS)_2]$, and $[Cu_2(L^1)(OMe)_2(MeCN)_2][BPh_4]_2$," *Journal of the Chemical Society, Dalton Transactions*, no. 12, pp. 2995–3003, 1988.
- [46] F. E. Mabbs, "Some aspects of the electron paramagnetic resonance spectroscopy of *d*-transition metal compounds," *Chemical Society Reviews*, vol. 22, no. 5, pp. 313–324, 1993.
- [47] J. E. Weder, T. W. Hambley, B. J. Kennedy et al., "Anti-inflammatory dinuclear copper(ii) complexes with indomethacin. synthesis, magnetism and EPR spectroscopy. Crystal structure of the N,N-dimethylformamide adduct," *Inorganic Chemistry*, vol. 38, no. 8, pp. 1736–1744, 1999.
- [48] J. Stankowski, "Orbital dynamics of the CuX_n complex in solids," *Journal of Molecular Structure*, vol. 597, no. 1–3, pp. 109–119, 2001.
- [49] D. F. Evans, "The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance," *Journal of the Chemical Society*, vol. 2003–2005, 1959.
- [50] F. Hasanvand, N. Nasrollahi, A. Vajjed, and S. Amani, "Synthesis, spectroscopy and characterization of four alkoxo-bridged dinuclear copper(II) complexes containing 2-amino-4-methylpyridine or 2-amino-4-cyanopyridine as the ligands," *Malaysian Journal of Chemistry*, vol. 12, no. 1, pp. 27–32, 2010.
- [51] J. Manzur, H. Mora, A. Vega et al., "Copper(II) complexes with new polyodal ligands presenting axial-equatorial phenoxo bridges {2-[(bis(2-pyridylmethyl)-amino)methyl]-4-methylphenol, 2-[(bis(2-pyridylmethyl)-amino)methyl]-4-methyl-6-(methylthio)phenol}: examples of ferromagnetically coupled bi- and trinuclear copper(II) complexes," *Inorganic Chemistry*, vol. 46, no. 17, pp. 6924–6932, 2007.
- [52] D. Kovala-Demertzi, D. Skrzypek, B. Szymańska, A. Galani, and M. A. Demertzis, "EPR spectroscopic study of a dinuclear copper(II) complex of tolfenamic acid," *Inorganica Chimica Acta*, vol. 358, no. 1, pp. 186–190, 2005.
- [53] F. Hasanvand, R. Arab Ahmadi, and S. Amani, "Synthesis, spectroscopy and magnetic characterization of five dinuclear

copper(II) complexes with 2, 3 or 4-pyridinemethanol as the ligand," *Journal of Sciences, Islamic Republic of Iran*, vol. 23, no. 1, pp. 37–43, 2012.

- [54] Z. Fu and T. Chivers, "Two new high-nuclearity copper(II) chloride oligomers with herringbone stacking patterns synthesized by in situ templation," *Canadian Journal of Chemistry*, vol. 84, no. 2, pp. 140–145, 2006.

