Alkoxo-bridged dinuclear copper(II) complexes with 2-amino-3-bromo-5-methylpyridine or 2-amino-3-cyanopyridine as the ligand

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Abstract

The synthesis, spectroscopic and magnetic characterization of six new alkoxo-bridged dinuclear copper(II) complexes are described. All six compounds have the general formula $[Cu_2(L)_4(O-R)_2](A)_2$, in which R = CH_3 or CH_3CH_2, L = 2-amino-3-bromo-5-methylpyridine (abbreviated as L_1), 2-amino-3-cyanopyridine (abbreviated as L_2) and A = NO_3^- or ClO_4^-. The title compounds all consist of dinuclear units with bridging methoxo groups for $[Cu_2(L_1)_4(O-CH_3)_2](NO_3)_2$ (**C$_1$**), $[Cu_2(L_1)_4(O-CH_3)_2](ClO_4)_2$ (**C$_2$**), $[Cu_2(L_2)_4(O-CH_3)_2](NO_3)_2$ (**C$_3$**), $[Cu_2(L_2)_4(O-CH_3)_2](ClO_4)_2$ (**C$_4$**), and bridging ethoxo group for $[Cu_2(L_1)_4(O-C_2H_5)_5](ClO_4)_2$ (**C$_5$**), $[Cu_2(L_2)_4(O-C_2H_5)_2](ClO_4)_2$ (**C$_6$**), with two ligands linked to each copper via the pyridine N atom, providing a $Cu_2N_2O_2$ unit. All complexes have been synthesized in one-step reaction and characterized by elemental analysis, FTIR and electronic spectra and by magnetic properties. The compounds exhibit antiferromagnetic interaction at room temperature. The UV-Vis spectra show three absorption bands attributed to d-d transition of copper(II) ion, ligand→ metal charge transfer and $\pi \to \pi^*$ or $n \to \pi^*$ transitions of the ligand. The FTIR spectra indicate $Cu_2N_2O_2$ unit vibrations from 405 – 580 cm^{-1}. All complexes show a room temperature magnetic moment between 1.37-1.52 B.M. per copper atom. The X-band electron spin resonance (ESR) studies indicate a weak half-field band, which is characteristic of the copper(II)-copper(II) dimer observed at about 1660 gauss. The observation of this band strongly suggests that the hyperfine structure arises from a triplet spin species. The spectra of samples in DMF or DMSO frozen at liquid nitrogen temperature show typical $\Delta m = 1$ transition.

Keywords: dinuclear copper(II) complexes; spin-spin interaction; spin-coupling

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Introduction

There has been considerable interest in defining the geometric, magnetic properties and electronic structure of the coupled dinuclear copper(II) complexes [1-6]. In the reported dinuclear copper(II) complexes, the exchange interaction between the unpaired electrons of

the two copper(II) atoms is carried out through either a σ-type pathway such as hydroxo bridge [4, 7], alkoxo bridge [2, 7], carboxylato bridge [3], mixed alkoxo and carboxylato bridge [5], or a π-type pathway like some extended π-conjugated aromatic bridges [8, 9]. It was found that the Cu-Cu diatance of the two adjacent copper(II) atoms in a σ-type pathway is not longer than 3.2 Å [10-12] and that in the π-type one can be extended to 6.0 Å [8]. A shorter Cu-Cu distance in the σ-type pathway can increase the intramolecular magnetic coupling. Also, it is found that the isotropic exchange parameter, 2J, is linearly related to the Cu-O-Cu bridging angle φ, [13, 14] and this correlation has been explained in terms of molecular-orbital theory [15]. It should be noted, however, that while φ is very important, but it is not the only structural parameter which can affect the value of 2J. Sinn and co-workers have demonstrated that the distortion from planar towards tetrahedral environment at the metal center, also markedly affect the magnitude of 2J, although they may not change its sign [16-22]. Another factor contributing to the magnitude 2J is the effect of changing the electron density at the bridging atoms [23]. McWhinnie reported the magnetic moment of a series of alkoxo-bridged complexes of the type $[Cu_2(ap)_4(OR)_2](NO_3)_2$, where ap = 2-aminopyridine [24, 25]. Unfortunately, no structural and magnetic studies are available for these complexes. Several investigations have been performed on alkoxo-bridged complexes of the type $[CuX(OR)]_2$, where ROH = an aminoalcohol and X = a uninegative ligand such as Br^- [26, 27]. In this series, no linear relationship between φ and 2J value has been found, presumably because in some of these complexes Cu_2O_2 ring is strongly distorted from planarity while in others the neighboring dimeric units are so close that they are able to form tetramers [28-32]. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of the Cu(II)-Cu(II) coupling in these systems is still imperfect. We have been interested the effects of changing the ligand and R group on the bridging oxygen will change the magnetic properties of dicopper(II) complexes. In the present study, six dinuclear copper(II) complexes are reported with 2-amino-3-bromo-5-methylpyridine or 2-amino-3-cyanopyridine ligands of the general formula $[Cu_2(L)_4(O-R)_2]^{+2}$, where L is 2-amino-3-bromo-5- methylpyridine or 2-amino-3-cyanopyridine, and R is either a methyl or ethyl group.

Experimental:
All chemicals were of reagent grade quality and were purchased from Merck Chemical Company and used as received without further purification.

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

Complex [Cu$_2$(L$_1$)$_4$(O-CH$_3$)$_2$](NO$_3$)$_2$; (C$_1$):
2 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ and 4.1 mmol of 2-amino-3-bromo-5-methylpyridine each dissolved in 15 ml of CH_3OH. 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. The product was separated after standing for one week. Yield ca. ≈ 65%.
Elemental analysis for $Cu_2C_{26}H_{34}N_{10}Br_4O_8$; (C$_1$); Found: C, 29.68; H, 3.42; N, 13.60; Cu, 11.75 %. Cal.; C, 29.42; H, 3.23; N, 13.20; Cu, 11.97 %.

Complex [Cu$_2$(L$_1$)$_4$(O-CH$_3$)$_2$](ClO$_4$)$_2$; (C$_2$):
1 mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ and 2.05 mmol of 2-amino-3-bromo-5-methylpyridine each dissolved in 15 ml of CH_3OH. 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. The product was separated after standing for one week. Yield ca. ≈ 43%.

Elemental analysis for $Cu_2C_{26}H_{34}N_8Br_4Cl_2O_{10}$; (**C$_2$**); Found: C, 28.11; H, 3.23; N, 9.52; Cu, 11.73 %. Cal.; C, 27.48; H, 3.02; N, 9.86; Cu, 11.19 %.

Complex [Cu$_2$(L$_2$)$_4$(O-CH$_3$)$_2$](NO$_3$)$_2$; (C$_3$):
This compound was obtained by similar procedure as reported for complex (**C$_1$**), using 2-amono-3-cyanopyridine as the ligand. Yield ca. ≈ 71%.
Elemental analysis for $Cu_2C_{26}H_{26}N_{10}O_8$; (**C$_3$**): Found: C, 43.13; H, 3.47; N, 18.93; Cu, 16.89 %. Cal.; C, 42.57; H, 3.57; N, 19.09; Cu, 17.32 %.

Complex [Cu$_2$(L$_1$)$_4$(O-CH$_3$)$_2$](ClO$_4$)$_2$; (C$_4$):
This complex was obtained by similar procedure as reported for complex (**C$_2$**), using 2-amono-3-cyanopyridine as the ligand. Yield ca. ≈ 39%.
Elemental analysis for $Cu_2C_{26}H_{26}N_8Cl_2O_{10}$; (**C$_4$**); Found: C, 37.75; H, 3.66; N, 14.28; Cu, 16.12 %. Cal.; C, 38.62; H, 3.24; N, 13.86; Cu, 15.72 %.

Complex [Cu$_2$(L$_1$)$_4$(O-C$_2$H$_5$)$_2$](ClO$_4$)$_2$; (C$_5$):
This complex obtained by similar method as described for (**C$_2$**), using C_2H_5OH and 2-amni-3-bromo-5-methylpyridine as the solvent and ligand, respectively. Yield ca. ≈ 42%.
Elemental analysis for $Cu_2C_{28}H_{38}N_8Br_4Cl_2O_{10}$; (**C$_5$**); Found: C, 29.04; H, 3.09; N, 10.33; Cu, 11.40 %. Cal.; C, 28.89; H, 3.29; N, 9.62; Cu, 10.92 %.

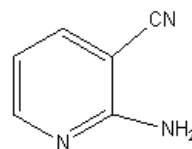*Complex [Cu$_2$(L$_2$)$_4$(O-C$_2$H$_5$)$_2$](ClO$_4$)$_2$; (C$_6$):*
This compound was obtained by similar method as described for (**C$_2$**), using C_2H_5OH and 2-amnino-3-cyanopyridine as the solvent and ligand, respectively. Yield ca. ≈ 47%.
Elemental analysis for $Cu_2C_{28}H_{30}N_8Cl_2O_{10}$; (**C$_6$**); Found: C, 39.53; H, 3.84; N, 14.05; Cu, 14.69 %. Cal.; C, 40.20; H, 3.61; N, 13.39; Cu, 15.19 %.
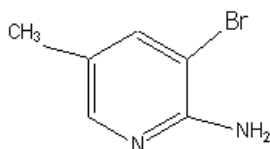
I= 2-amino-3-bromo-5-methylpyridine   II= 2-amino-3 -cyanolpyridine
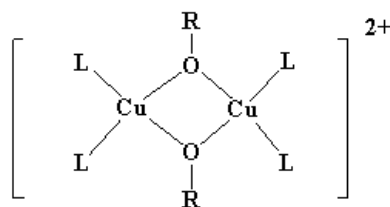
R= CH$_3$, CH$_3$CH$_2$
L= **I** or **II**

Physical measurements: C, H and N determination were made at the Research Institute of the Petroleum Industry of Iran. Cu determination was carried on a Perkin-Elmer Atomic Absorption spectrophotometer at the wavelength of 324.7 nm. Electronic spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. FTIR spectra were obtained in the 4000-400 cm^{-1} range

as KBr disks using a Spectrum 1000 Perkin-Elmer 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 both at room and at liquid nitrogen temperatures in DMF or in DMSO on an IBM electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. A Johnson Matthey Alfa products magnetic susceptibility balance was used to measure the room temperature magnetic moments.

Results and Discussion

Electronic Spectra: The spectroscopic data for all complexes are presented in Table 1. The electronic spectra of all compounds were obtained from a solid sample using the diffuse reflectance technique and are very similar, thus illustrating similar geometries between the complexes. The compounds show a broad band at 734 nm for complex (C_1), 702 nm for complex (C_2), 712 nm for complex (C_3), 711 nm for complex (C_4), 722 nm for complex (C_5) and 731 nm for complex (C_6) due to the ligand field transition for the CuN_2O_2 chromophore [33, 34]. The second absorption bands at 316, 320, 330, 325, 329 and 321 nm for compounds C_1, C_2, C_3, C_4, C_5 and C_6, respectively, are assigned to charge transfer from the non-bonding orbital of bridging-oxygen atoms to the vacant copper(II) d orbitals [33, 35]. The last absorption band observed at 275, 285, 259, 248, 260 and 262 nm for of complexes C_1, C_2, C_3, C_4, C_5 and C_6, respectively, are due to $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [36].

Table1. Spectroscopic data for all six complexes.

Complex	Absorption (nm)	IR(Cu-O) IR(Cu-N) (cm^{-1})	ESR Half-field	ESR Powder	ESR Solution in DMF	μ_{Cu}(R.T.) B.M.
(C_1)	734, 316, 275	565, 515, 405	g_h= 4.07	g = 2.06	$g_{\parallel}$ = 2.28 $A_{\parallel} \approx 160$ $A_{N\perp} \approx 15$	1.45
(C_2)	702, 320, 285	548, 510, 430	g_h= 4.11	g = 2.06	$g_{\parallel}$ = 2.28 $A_{\parallel} \approx 163$ $A_{N\perp} \approx 15$	1.48
(C_3)	712, 330, 259	580, 547, 443	g_h= 4.13	g = 2.07	$g_{\parallel}$ = 2.30 $A_{\parallel} \approx 165$ $A_{N\perp} \approx 15$	1.37
(C_4)	711, 325, 248	530, 503, 415	g_h= 4.04	g = 2.06	$g_{\parallel}$ = 2.32 $A_{\parallel} \approx 160$ $A_{N\perp} \approx 15$	1.42
(C_5)	722, 329, 260	574, 536, 421	Not found	g = 2.05	$g_{\parallel}$ = 2.24 $A_{\parallel} \approx 182$ $A_{N\perp} \approx 15$	1.43
(C_6)	731, 321, 262	551, 490, 423	Not found	g = 2.06	$g_{\parallel}$ = 2.27 $A_{\parallel} \approx 180$ $A_{N\perp} \approx 15$	1.52

Infrared spectra: The FTIR spectra were studied in detail, given the symmetry of the molecule. For the $Cu_2O_2L_4$ kind of complexes with D_{2h} symmetry, two important modes of B_{2u} and B_{3u}, associated with the vibration of the Cu_2O_2 unit were expected. This would potentially be of great help in the purpose of verifying the dinuclear structure for this type of compound [37-40]. The frequency of these modes is affected by the Cu_2O_2 planarity and the angle of the Cu-O-Cu ring [41-44]. The IR spectra of the free ligand and the complexes were obtained in the range of 4000-400 cm^{-1}. All the bands present in the free ligands are also observed in the spectra of the complexes. The IR spectra of the present compounds are of particular interest in studying the Cu_2O_2 ring. For Cu-alkoxo bridged compounds, the Cu-O and Cu-N vibrations are generally found between 580-400 cm^{-1} [45-49]. The magnetic moment and electron spin resonance (ESR) of these complexes are known to be dimeric with the room temperature magnetic moment between 1.37-1.52 B.M. per copper, which appears to be low for a d^9 configuration. This suggests the presence of a strong spin-spin interaction through the bridging ligands [50]. To provide further supporting evidence for the presence of a strong antiferromagnetic interaction, magnetic susceptibility measurements were determined for the complex (**C$_2$**) in the range of 5- 270 K. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal's constants [51]. Graphical magnetic properties of this complex at various temperatures are shown in Figures 1-3. Plot of μ_{Cu} versus T indicates magnetic moment decreases as the temperature lowered and this behavior is the characteristic of spin-spin interaction through bridging system [52]. The corrected susceptibility data were fitted using the modified Bleaney-Bowers equation for exchange-coupled pairs of copper(II) ions [53].

$$\chi_m = (2Ng^2\beta^2 / kT)[3 + \exp(-2J / kT)]^{-1}(1-\rho) + \chi_{\rho\times}\rho \qquad (1)$$

Where ρ is the percentage of paramagnetic impurity in the sample, N, g, β, k and T have their usual meanings. The singlet-triplet energy gap (–2J) is defined by the Hamiltonian **H$_{ex}$ = –2JS$_1$S$_2$**. The fit was performed by means of non-linear least-squares procedure. The fitting converged at $2J = -120$ cm^{-1} and $g = 2.02$ with $\rho = 2.16 \times 10^2$ c.g.s. unit
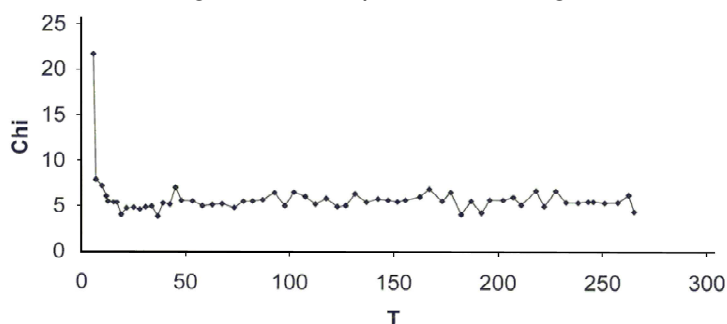

Fig. 1. A plot of chi ($\chi_{Cu} \times 10^{+4}$) versus T for complex (C$_2$).

X-band powder and frozen solution ESR spectra of all complexes were measured at both liquid nitrogen and room temperatures. In the solid state, the spectra were similar and appear to be ESR silent, with only a weak signal due to monomeric impurity ($g = 2.06$) being present. The observed frozen solution ESR spectra of all compounds in DMF or DMSO is typical for dinuclear copper(II) complexes. A weak $\Delta m = 2$ transition for all compounds was observed, thus confirming the Cu….Cu magnetic exchange interaction at half-field, which is characteristic of the dimeric unit [54, 55].
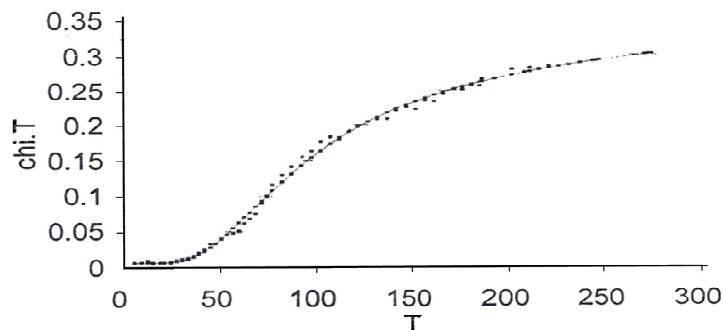
Fig. 2. A plot of $\chi_{Cu} \times T$ versus T for complex (C_2).
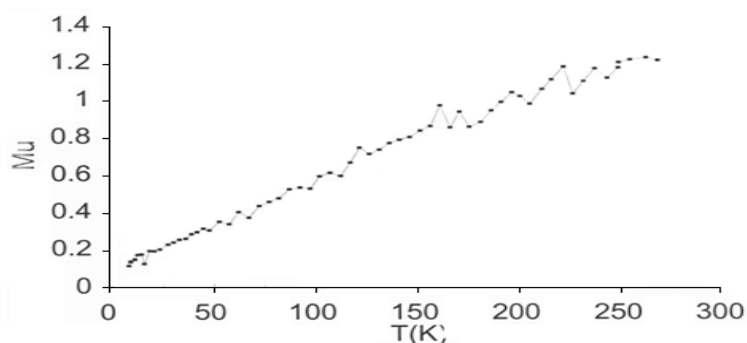
Fig. 3. A plot of magnetic moment (μ_{Cu}) versus T for complex (C_2).

The dinuclear copper(II) complex has a $g_{\parallel}$ value of ≈ 2.28 with an $A_{\parallel}$ value of ≈ 170 gauss and is in agreement with a $d_{x^2-y^2}$ ground state in a square-pyramidal geometry [56,57]. The $A_{N\perp}$ value of ≈ 15 gauss and the presence of five peaks for the nitrogen superhyperfine structure for the complexes agrees with two N donors per copper(II) ion.

Conclusion

In summary, six alkoxo-bridged dinuclear copper(II) complexes with 2-amino-3-bromo-5-methylpyridine or 2-amino-3-cyanopyridine as the ligands have been made in a one-step synthesis and were spectroscopically characterized. All compounds show a subnormal magnetic moment between 1.37-1.52 B.M. per copper at room temperature, suggesting an antiferromagnetic spin-exchange interaction within each molecule. The X-band ESR spectrum of the complexes in a DMF or DMSO glass (77 K) shows a $g_{\parallel}$ value of ≈ 2.28 with an $A_{\parallel}$ value of ≈ 170 gauss, which is typical of dimeric square-pyramidal copper(II) complexes with a $d_{x^2-y^2}$ ground state.

Acknowledgments

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