

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

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Abstract : Four complexes of the type $[\text{Cu}_2(\text{L})_4(\text{OR})_2](\text{X})_2$, where L is 2-amino-4-methylpyridine or 2-amino-4-cyanopyridine and $\text{X} = \text{Cl}^-$, have been synthesized. The title compounds all consist of dinuclear units with OCH_3 or OC_2H_5 bridging groups. All complexes were synthesized in a one-step reaction, and were characterized by elemental analysis, FTIR, ESR, electronic spectroscopy and by magnetic moment determination. The compounds exhibit antiferromagnetic interactions at room temperature. The UV-Vis spectra show three absorption bands attributed to the d-d transition of the copper(II) ion, ligand→metal charge transition (LMCT) and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand. The FTIR spectra exhibit Cu_2O_2 ring vibrations from $570\text{--}410\text{ cm}^{-1}$. All complexes show room temperature magnetic moments of about 1.32 to 1.54 B.M. per copper atom. The X-band electron spin resonance (ESR) studies indicate a weak half-field band, which is characteristic of the Cu(II)–Cu(II) dimer, observed at about 1600 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.

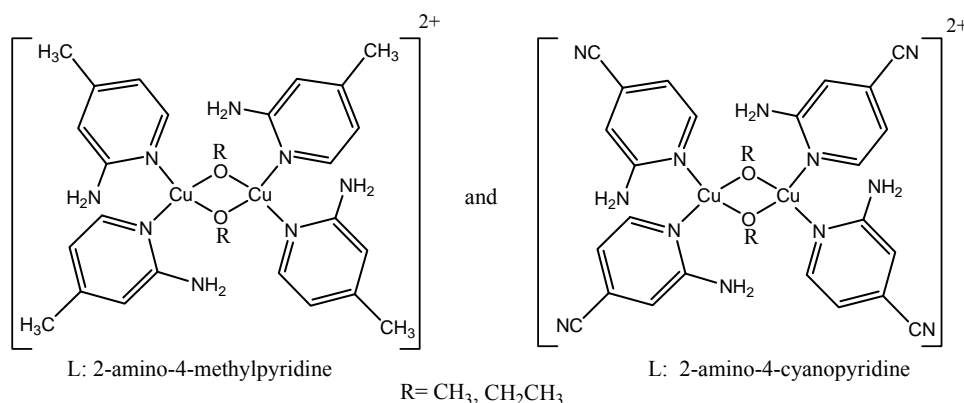
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Introduction:

Many inorganic molecules are known to contain more than one metal atom. Such entities are commonly termed "polynuclear" complexes. The polynuclear metals are often embedded in or supported by a ligand matrix. The magnetic behavior of polynuclear complexes can be estimated by such factors as the electronic structure of the bridging and end-capping ligands and of the complexes [1, 2]. The ligand has a great influence on the metal–metal interaction [3, 4]. The structural and magnetic properties of many dinuclear compounds containing the Cu_2O_2 system have been previously investigated to explain the influence of spin–spin interactions through the bridging system [5-10]. It is now generally accepted that the spin–spin coupling in these complexes occurs through the bridging groups by a pathway in the square–planar oxygen–bridged compounds of the type $[\text{Cu}_2(\text{L})_4(\text{O-R})_2]^{+2}$, where L = monodentate ligand. It is found that the isotropic exchange parameter, $2J$, is linearly related to the Cu–O–Cu bridging angle, θ , [5, 6] and this correlation has been explained in terms of molecular orbital

theory [11]. It should be noted, however, that although θ is very important, it is not the only structural parameter that can affect the value of $2J$. Sinn and co-workers have shown that the distortion from planar to a tetrahedral environment at the metal center also markedly influences the magnitude of $2J$ [12-15]. Another factor contributing to the magnitude of $2J$ is the effect of changing the electron density at the bridging atoms [16]. The systematic study of small coordination compounds has already given a more detailed understanding of the magnetic exchange phenomenon. Furthermore, a relationship between the structures of the complexes and their magnetic properties could be established. In particular, dinuclear copper(II) complexes have been found to be very useful, considering the relatively simple single ion properties of the copper(II) ion that facilitates the interpretation of the magnetic data. The simplest bridging systems used are monoatomic bridges, such as hydroxo [17-19], alkoxo [20, 21], chloro [22-25], bromo [26-28], fluoro [29, 30], azido [31, 32] and thiolato [33, 34]. The most extensively studied series of compounds are



represented by the planar dihydroxo-bridged dinuclear copper(II) complexes. These investigations have resulted in important insights in the superexchange mechanism taking place via double monoatomic bridges. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of the copper(II)-copper(II) coupling is still imperfect. We have been interested in how 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, four dinuclear copper(II) complexes are reported with 2-amino-4-methylpyridine or 2-amino-4-cyanopyridine ligands of the general formula $[\text{Cu}_2(\text{L})_4(\text{OR})_2]^{2+}$, where L is 2-amino-4-methylpyridine or 2-amino-4-cyanopyridine, and R is either a methyl or ethyl group.

Proposed structure for all four complexes

Experimental

Chemicals.

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 $[\text{Cu}_2(2\text{-amino-4-cyanopyridine})_4(\text{OCH}_3)_2]\text{Cl}_2$; (**C₁**):

0.341 g (2 mmol) of copper(II) chloride dihydrate and 0.488 g (4.1 mmol) of 2-amino-4-cyanopyridine 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, and the solution was filtered to remove any solids. The product was separated

after standing for one week. Yield ca. \approx 0.52 g (about 70%).

Elemental analysis for $\text{Cu}_2\text{C}_{26}\text{H}_{26}\text{N}_{12}\text{Cl}_2\text{O}_2$; (**C₁**); Found: C, 41.96; H, 3.27; N, 23.72; Cu, 16.52%. Calc.; C, 42.40; H, 3.56; N, 22.82; Cu, 17.26%.

Complex $[\text{Cu}_2(2\text{-amino-4-methylpyridine})_4(\text{OCH}_3)_2]\text{Cl}_2$; (**C₂**) was obtained by a similar method as described for compound (**C₁**). Yield ca. \approx 0.54 g (about 78%).

Elemental analysis for $\text{Cu}_2\text{C}_{26}\text{H}_{38}\text{N}_8\text{Cl}_2\text{O}_2$; (**C₂**); Found: C, 45.81; H, 5.37; N, 17.42; Cu, 17.84%. Calc.; C, 45.09; H, 5.53; N, 16.18; Cu, 18.35%.

Complex $[\text{Cu}_2(2\text{-amino-4-cyanopyridine})_4(\text{OC}_2\text{H}_5)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**C₃**):

0.341 g (2 mmol) of copper (II) chloride dihydrate and 0.443 g (4.1 mmol) of 2-amino-4-cyanopyridine each dissolved in 25 ml of $\text{C}_2\text{H}_5\text{OH}$. The Cu(II) salt solution was then added slowly to the 2-amino-4-cyanopyridine solution, thereby preventing any precipitation and filtered to remove any solids. After standing for two weeks, the products were separated. Yield ca. \approx 0.26 g (about 34%).

Elemental analysis for $\text{Cu}_2\text{C}_{28}\text{H}_{34}\text{N}_{12}\text{Cl}_2\text{O}_2$; (**C₃**); Found: C, 42.91; H, 4.17; N, 21.53; Cu, 16.12%. Calc.; C, 42.00; H, 4.28; N, 20.99; Cu, 15.87%.

Complex $[\text{Cu}_2(2\text{-amino-4-methylpyridine})_4(\text{OC}_2\text{H}_5)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**C₄**) was obtained by a similar method as described for compound (**C₃**). Yield ca. \approx 0.28 g (about 39%).

Elemental analysis for $\text{Cu}_2\text{C}_{28}\text{H}_{44}\text{N}_8\text{Cl}_2\text{O}_2$; (**C₄**); Found: C, 46.11; H, 5.87; N, 14.77; Cu, 17.43%. Calc.; C, 45.53; H, 6.00; N, 15.17; Cu, 17.20%.

Physical measurements.

C, H and N determinations were made at the Research Institute of the Petroleum Industry of Iran. Cu determination was carried on a Perkin-

Elmer Atomic Absorption spectrophotometer. 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 compounds are presented in Table 1. The electronic spectra of all complexes 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 561 nm for complex (C_1), 560 nm for complex (C_2), 643 nm for complex (C_3) and 689 nm for complex (C_4) due to the ligand field transition for the CuN_2O_2 chromophore [35, 36]. The second absorption bands at 318, 352, 313 and 385 nm for compounds C_1 , C_2 , C_3 and C_4 , respectively, are assigned to charge transfer from the non-bonding orbital of bridging-oxygen atoms to the vacant copper(II) d orbitals [35, 37]. The last absorption band observed at about 240 nm for each of the complexes is associated with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [38].

Table1: Spectroscopic data for all four complexes.

Complex	Absorption (nm)	$\nu(\text{Cu-O})$ $\nu(\text{Cu-N})$ (cm^{-1})	ESR Half-field	ESR Powder	ESR Solution in DMF	$\mu_{\text{Cu}}(\text{R.T.})$ B.M.
(C_1)	561, 318, 246	568, 530, 423	$g_h = 4.12$	$g = 2.06$	$g_n = 2.29$ $A_n \approx 165$ $A_{N_L} \approx 15$	1.37
(C_2)	560, 352, 245	556, 534, 474	$g_h = 4.18$	$g = 2.06$	$g_n = 2.28$ $A_n \approx 170$ $A_{N_L} \approx 15$	1.32
(C_3)	643, 313, 240	573, 531, 414	$g_h = 4.09$	$g = 2.07$	$g_n = 2.31$ $A_n \approx 165$ $A_{N_L} \approx 15$	1.54
(C_4)	689, 385, 235	538, 437, 410	$g_h = 4.16$	$g = 2.06$	$g_n = 2.30$ $A_n \approx 180$ $A_{N_L} \approx 15$	1.45

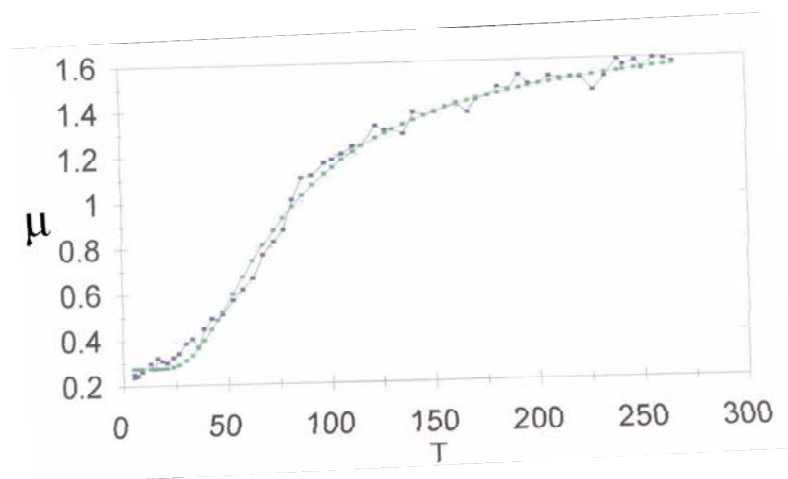


Figure 1 : Magnetic moment (μ) of complex (C_3) versus T(K)

Infrared spectra.

The FTIR spectra were studied in detail, given the symmetry of the molecule. For the $Cu_2O_2L_4$ kind of compounds 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 for the purpose of verifying the dinuclear structure for this type of compound [39-42]. The frequency of these modes is affected by the Cu_2O_2 planarity and the angle of the Cu-O-Cu units [43-46]. The IR spectra of the free ligand and the complexes were obtained in the range of $4000-400\text{ cm}^{-1}$. 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 square-planar Cu-alkoxo bridged compounds, the Cu-O and Cu-N vibrations are generally found between $580-400\text{ cm}^{-1}$ [47-49]. According to the magnetic moment data, these complexes are known to be dimeric with the room temperature magnetic moment between 1.32-1.54 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_3) 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]. The graphical magnetic moment representation of this complex at various temperatures shown in Figure 1 for μ_{Cu} versus T. The 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].

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

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 $H_{ex} = -2JS_1S_2$. The fit was performed by means of non-linear least-squares procedure. The fitting converged at $2J = -135\text{ cm}^{-1}$ and $g = 2.02$ with $\rho = 2.32 \times 10^{-2}$ c.g.s. units.

X-band powder and frozen solution ESR spectra of all compounds were obtained 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 [53]. The dinuclear copper(II) complex has a g_{II} value of ≈ 2.28 with an A_{II} value of ≈ 165 gauss and is in agreement with a $d_{x^2-y^2}$ ground state in a square-pyramidal geometry [54, 55]. 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.

Conclusions

In summary, four bis-(μ -alkoxo)-bridged dinuclear copper(II) complexes with 2-amino-4-cyanopyridine or 2-amino-4-methylpyridine as the ligands have been made in a one-step synthesis and were spectroscopically characterized. All complexes show a subnormal magnetic moment between 1.32-1.54 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_{II} value of ≈ 2.28 with an A_{II} value of ≈ 165 gauss, which is typical of dimeric square-pyramidal copper(II) complexes with a $d_{x^2-y^2}$ ground state.

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