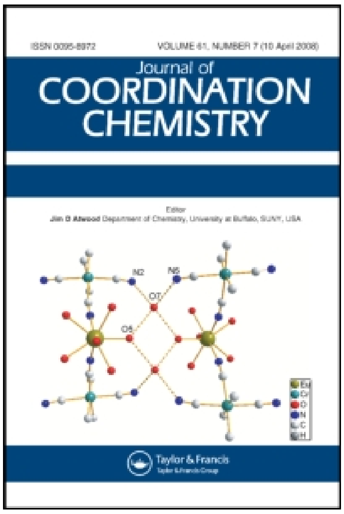

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Two new alkoxo-bridged dinuclear copper(II) complexes with 3-aminopyrazidine-2-carboxylic acid as ligands

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Two new alkoxo-bridged dinuclear copper(II) complexes with 3-aminopyrazidine-2-carboxylic acid as ligands

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The synthesis, spectroscopic and magnetic properties of two new alkoxo-bridged dinuclear copper(II) complexes are described. Both compounds have the general formula $[Cu(\mu\text{-}OR)(L)_2]_2X_2 \cdot H_2O$, in which $\mu\text{-}OR = CH_3O^-$ or $C_2H_5O^-$, L = 3-aminopyrazidine-2-carboxylic acid and $X = NO_3^-$. The title complexes consist of a dinuclear unit with bridging methoxo for $[Cu(\mu\text{-}OCH_3)(L)_2]_2(NO_3)_2 \cdot H_2O$ (**1**) and bridging ethoxo for $[Cu(\mu\text{-}OC_2H_5)(L)_2]_2(NO_3)_2 \cdot H_2O$ (**2**) with two ligands linked to each copper via pyrazidine N atom, providing a square pyramidal CuN_2O_2 unit. Both compounds have been synthesized in a one-step reaction and characterized by elemental analysis, FTIR, ESR, electronic spectra and by room temperature magnetic moments. The compounds exhibit antiferromagnetic interaction at room temperature. The UV-vis spectra show three absorption bands, attributed to d–d transitions of copper, ligand → metal charge transfer and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of ligand. The FTIR spectra indicate Cu_2O_2 ring vibration in 570–450 cm^{-1} range. Both complexes show a room temperature magnetic moment of about 1.50 B.M. per copper atom. The X-band electron spin resonance (ESR) studies indicate a weak half-field band, 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 spin triplet species. The spectrum of frozen samples in DMF or in DMSO at liquid nitrogen temperature shows a typical $\Delta m = 1$ transition.

Keywords: Dinuclear copper(II) complexes; Di-alkoxo bridged; Spin–spin interaction

1. Introduction

The structural and magnetic properties of many dinuclear compounds containing Cu_2O_2 system have been investigated to understand the spin–spin interaction through the bridging system [1–7]. It is accepted that spin coupling in these complexes occurs through the bridging groups in square planar oxygen-bridged compounds of the type $[Cu_2(L)_4(OR)_2]^{+2}$, where (L = monodentate ligand). It is found that the isotropic exchange parameter, $-2J$, is linearly related to the Cu–O–Cu bridging angle, ϕ [1, 2, 8]. This correlation has been explained in terms of molecular orbital theory [9]. It should be noted, however, that while ϕ is very important, it is not the only structural parameter which can affect the value of $-2J$. Sinn and co-workers have demonstrated that distortion from planar towards tetrahedral at the metal center also markedly affects the

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magnitude of $-2J$ [10–13]. Another factor contributing to the magnitude of $-2J$ is the effect of changing electron density at the bridging atom [14]. Four decades ago, McWhinnie reported the magnetic moment of a series of alkoxide-bridged complexes of the type $[Cu_2(ap)_4(OR)_2](NO_3)_2$, where (ap = 2-aminopyridine) [15, 16]. Unfortunately, no structural or 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^-) [17, 18]. In this series no linear relationship between ϕ and $-2J$ value has been found [19]. Dinuclear copper(II) sites play an important role in biological metalloproteins. The best investigated dinuclear copper(II) proteins are hemocyanin [20], tyrosinase [21, 22], or catheolase [23]. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of copper(II)–copper(II) coupling is still imperfect. We have been interested in the effects of changing the R group on the bridging oxygen with change in magnetic properties. The present work reports a one-step synthesis of two new dinuclear copper(II) complexes, spectral studies, and the magnetic moments from reactions of copper(II) nitrate trihydrate with 3-aminopyrazidine-2-carboxylic acid.

2. Experimental

2.1. *Chemicals*

All chemicals were of reagent grade purchased from Merck Chemical Company and used as received without further purifications.

2.2. *Preparation of the complexes*

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

$[Cu_2(\mu\text{-}OCH_3)_2(L)_4](NO_3)_2 \cdot H_2O$ (1). 2 mmol of copper(II) nitrate trihydrate and 4 mmol of ligand each dissolved in 25 mL of CH_3OH. The Cu(II) salt solution was then added slowly to the ligand solution, preventing any precipitation, filtered to remove any solids and after a day the product separated. Yield ca ≈70%.

Elemental analysis for $[Cu_2(\mu\text{-}OCH_3)_2(L)_4](NO_3)_2 \cdot H_2O$ (**1**); Found: C, 30.04; H, 3.26; N, 21.47; Cu, 14.43%. Calcd: C, 29.77; H, 3.18; N, 22.09; Cu, 14.34%.

$[Cu_2(\mu\text{-}OC_2H_5)_2(L)_4](NO_3)_2 \cdot H_2O$ (2). It was obtained by a similar method as described for **1**. Yield ca ≈60%.

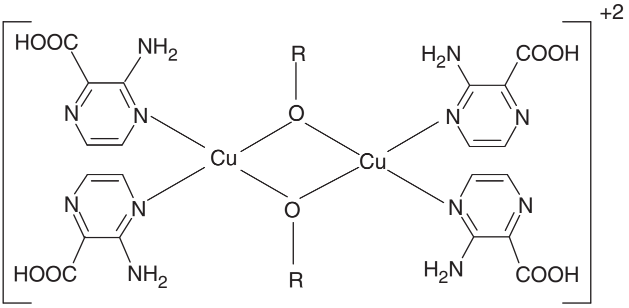
Elemental analysis for $[Cu_2(\mu\text{-}OC_2H_5)_2(L)_4](NO_3)_2 \cdot H_2O$ (**2**); Found: C, 31.12; H, 3.49; N, 19.76; Cu, 13.91%. Calcd: C, 30.57; H, 3.57; N, 21.69; Cu, 14.06%.

2.3. *Physical measurements*

C, H and N were determined at the Research Institute of Petroleum Industry of Iran. Cu determination was carried on a Perkin-Elmer Atomic Absorption

Table 1. Spectroscopic data for **1** and **2**.

Complex	Absorption (nm)	IR(anion) (cm^{-1})	IR(Cu–O) (cm^{-1})	ESR half-field	ESR powder	ESR solution in DMF	μ_{Cu} (R.T.) B.M.
1	639, 342, 240	1368, 819, 709	565, 456	$g_h = 4.12$	$g = 2.06$	$g_\parallel = 2.31$ $A_\parallel \approx 165$ $A_{n\perp} \approx 15$	1.53
2	557, 352, 245	1377, 838, 819	557, 448	$g_h = 4.18$	$g = 2.06$	$g_\parallel = 2.27$ $A_\parallel \approx 160$ $A_{N\perp} \approx 15$	1.48



Scheme 1. Proposed structure of $[Cu_2(L)_4(OR)_2]^{+2}$.

spectrophotometer at 324.7 nm. Electronic spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. FTIR spectra were made in the 4000–300 cm^{-1} range as KBr disks using a Perkin-Elmer Spectrum 1000. The spectra were calibrated using polystyrene bands at 3028, 1601 and 1208 cm^{-1}. X-band electron paramagnetic resonance spectra were recorded on powders and frozen solutions of the complexes 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.

3. Results and discussion

3.1. *Electronic spectra*

The spectroscopic data for all compounds are presented in table 1. The electronic spectra obtained from a solid sample using the diffuse reflectance technique are very similar, illustrating similar geometry. The compounds show a broad band at 639 nm for **1** and 557 for **2**, due to the d–d transition for a CuN_2O_2 chromophore [24, 25]. The second absorption bands at 342 nm for **1** and 352 nm for **2** are assigned to charge transfer from the non-bonding orbital of bridging-oxygen atoms to half-filled $d_{x^2-y^2}$ orbital of the copper(II) [24, 26]. The final absorption band at about 240 nm for **1** and 245 nm for **2** are associated with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [27].

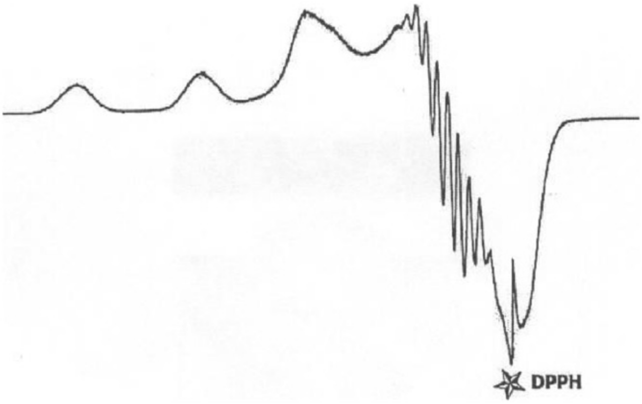


Figure 1. Frozen solution (77 K) ESR X-band spectra of complex **1**. * denotes DPPH maker ($g = 2.0036$).

3.2. *Infrared spectra*

The IR spectra were studied in some detail, given the symmetry of the molecule. For $Cu_2O_2L_4$ with D_{2h} symmetry, two important modes, B_{2u} and B_{3u}, associated with the vibration of Cu_2O_2 unit provide verification of the dinuclear structure for this type of compound [28–31]. The frequency of these modes is affected by the Cu_2O_2 planarity and the angle Cu–O–Cu units [32–35]. For square-planar-Cu-alkoxo bridged compounds, Cu–O vibrations are reported between 580–450 cm^{-1} [36–38]. The bands at about 1360(vs), 820(s) and 710(s) cm^{-1} are attributed to ionic nitrate for ν_3, ν_2 and ν_4, respectively [39]. All bands present in the free ligand are also observed in the spectrum of complexes.

3.3. *Magnetic moment and electron spin resonance*

Both complexes are dimeric with the room temperature magnetic moment between 1.45–1.55 B.M. per copper, low for a d^9 configuration, so there must be a strong spin–spin interaction through the bridging ligands [40]. In order to provide further supporting evidence for a strong antiferromagnetic interaction, X-band powder and frozen solution ESR spectra of all compounds were obtained at liquid nitrogen and at 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 ($g = 2.06$) seen. The observed frozen solution ESR spectra of both compounds in DMF or DMSO is typical for dinuclear copper(II) complexes. A weak $\Delta m = 2$ transition for all compounds confirms the occurrence of a $Cu \cdots Cu$ magnetic exchange interaction at half-field, which is characteristic of the dimer (see figure 2) [41, 43]. The dinuclear copper(II) complex has a $g_{\parallel}$ value of ≈ 2.28 with $A_{\parallel}$ of ≈ 165 gauss, which is in agreement with a $d_{x^2-y^2}$ ground state and a square-pyramidal geometry [44–46]. The $A_{N\perp}$ value of ≈ 15 gauss and presence of nine peaks for nitrogen superhyperfine structure for the complexes agrees with two N donors per copper(II) (see figure 1).

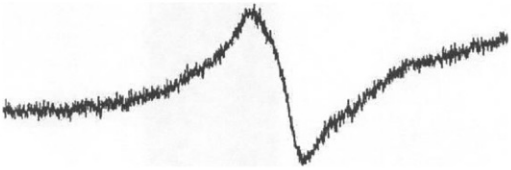


Figure 2. Frozen solution (77 K) ESR spectra of complex **1** at half-field (≈1600 gauss).

4. Conclusions

Two new *bis*-(μ-alkoxo)-bridged dinuclear copper(II) complexes with 3-aminopyrazidine-2-carboxylic acid have been made in a one-step synthesis and spectroscopically characterized. Both complexes show subnormal magnetic moment between 1.45–1.55 B.M. per copper at room temperature, suggesting an antiferromagnetic spin-exchange interaction within each molecule. The X-band ESR spectra of complexes in DMF or DMSO glass (77 K) show $g_{\parallel}$ value of ≈2.28 with $A_{\parallel}$ value of ≈165 gauss, typical of dimeric square-pyramidal copper(II) complexes with $d_{x^2-y^2}$ ground state.

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