

# SYNTHESIS OF BINUCLEAR MONOHYDROXO BRIDGED COPPER(II) COMPLEXES WITH 1,10-PHENANTHROLINE AND 4,4'-DIMETHYL-2,2'-BIPYRIDINE<sup>☆</sup>

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**ABSTRACT:** Two new compound of type  $[(\text{chelate})_2\text{Cu}-\text{OH}-\text{Cu}(\text{chelate})_2] X_3 \cdot n\text{H}_2\text{O}$ , where chelate=1,10-phenanthroline;  $X=\text{Cl}^-$  ( $n=3.5$ ) and chelate=4,4'-dimethyl-2,2'-bipyridine;  $X=\text{ClO}_4^-$  ( $n=5$ ) have been synthesised and their properties investigated. The complexes show room temperature magnetic moment order of 1.0 B.M. per copper atom. The X-band ESR spectrum of powdered samples at room temperature shows typical  $\Delta m=1$  transition at  $g_{\text{av}}=2.075$  for 1,10-phenanthroline and  $g_{\text{av}}=2.085$  for 4,4'-dimethyl-2,2'-bipyridine, and much weaker  $\Delta m=2$  transition at half-field which is the characteristic of dimeric unit.

**KEY WORDS:** Copper(II), Dinuclear and monohydroxo bridged.

Many inorganic molecules are known to contain more than one metal atom, such entities commonly termed "polynuclear". The polynuclear metals are embedded in or supported by the ligand matrix. The magnetic properties of polynuclear complexes are influenced by electronic structure of the ligand and the structure of the complexes [1]. Ligand has great influence on the metal-metal interaction. For example,  $\text{Cu}_2(\text{HCO}_2)_4(\text{pyridine})_2$  has a magnetic moment of 1.1 B.M. per atom at room temperature, while  $\text{Cu}_2(\text{CH}_3\text{-CO}_2)_4(\text{pyridine})_2$  has magnetic moment of 1.43 B.M. [2,3]. The same behavior is observed for the bridging group; metal ions interact much stronger with bromo-

bridged than chloro bridged [4,5].

In the last thirty years, there have been several investigations devoted to the synthesis of monohydroxy copper(II) complexes in the solution [6-10], the synthesis of copper(II) binuclear compounds and determination of their crystal structure, magnetic properties and stability constants [11-18].

The main reason for most of these works are better understanding of the exchange interactions. Many useful results have already been obtained. Hatfield et al. [19,20] found a linear relationship between the  $2J$  value (singlet-triplet) energy gap and Cu-O-Cu bridging angle. Later on, Theriot et al.

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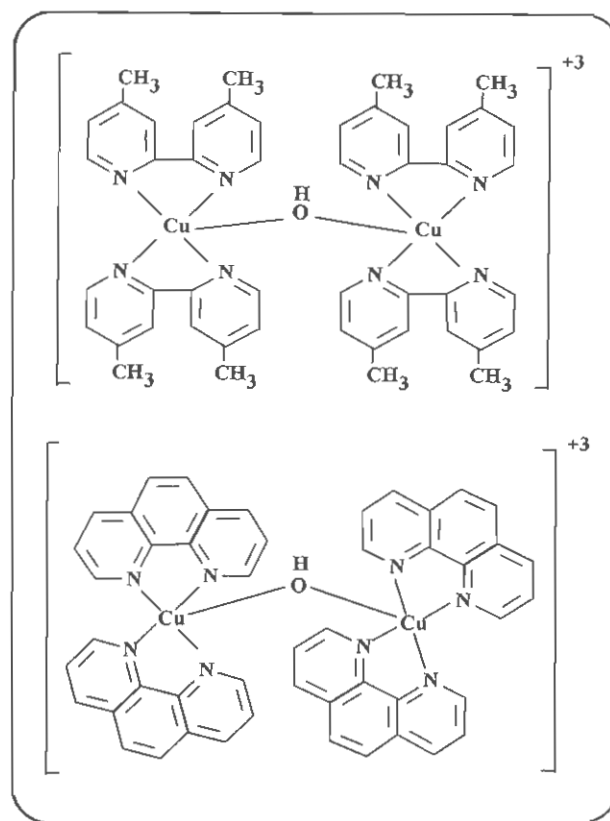
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found that changing the electron density at the bridge by use of the alkoxide complexes will have an influence on the  $2J$  value [21]. Binuclear copper(II) complexes with monohydroxy bridged are rare [22-27]. We know few of such complexes:  $[(tren)Cu(OH)Cu(tren)]x_3$ , where tren is 2,2',2"-triaminotriethylamine and  $x$  is  $PF_6^-$  or  $ClO_4^-$  and  $[(bipy)_2Cu(OH)Cu(bipy)_2](ClO_4)_3$  and  $[(phen)_2Cu(OH)Cu(phen)_2](ClO_4)_3$ , where bipy is 2,2'-bipyridine and phen is 1,10-phenanthroline [28]. Monohydroxy bridged copper(II) complexes show considerably greater antiferromagnetic interaction than the dihydroxy bridged copper(II) complexes. This is expected in that there is an appreciably larger Cu-O-Cu bridging angle in the monohydroxy bridged copper(II) complexes. In this paper, the synthesis and physical properties are reported for binuclear copper (II) complexes with monohydroxy bridged,  $[(chelate)_2Cu(OH)Cu(chelate)_2]x_3 \cdot nH_2O$ , where chelate is 1,10-phenanthroline and  $X=Cl^-$  ( $n=3.5$ ) and where chelate is 4,4'-dimethyl-2,2'-bipyridine and  $X=ClO_4^-$  ( $n=5$ ) (Scheme). The complexes with phen as a ligand has a magnetic moment of 1.48 B.M. at 296.4K. The moment drops down to 0.85 B.M. when the temperature is decreased to liquid nitrogen temperature. The other compound has a magnetic moment of 1.20 B.M. at 297.5K and 1.00 B.M. at liquid nitrogen temperature. Both compounds exhibit low magnetic moment at room temperature, which proves that there is a strong antiferromagnetic interaction between copper(II) at the ground state. The visible absorption spectra of the compounds in aqueous solution show  $\lambda_{max} = 635$  nm ( $\epsilon_{av} = 146$ ) for phen complex and  $\lambda_{max} = 620$  nm ( $\epsilon_{av} = 133$ ) for 4,4'-bipy complex. The very broad peak, around  $1600\text{ cm}^{-1}$  in the solution of the aquated  $[(chelate)_2Cu(OH)Cu(chelate)_2]^{+3}$  can be assigned to d-d transition [29].

The ESR spectra of the powdered samples at room temperature shows typical triplet state feature with  $\Delta m = \pm 1$  transition at  $g_{av} = 2.075$  for phen complex and  $g_{av} = 2.085$  for 4,4'-bipy complex and a much weaker  $\Delta m = 2$  transition at half-field, characteristic of the dimeric unit [30].

The KBr pellet IR spectrum of either two compounds shows a relatively strong intensity band at about  $3500\text{ cm}^{-1}$  and Cu-O frequency in the range of  $500\text{-}450\text{ cm}^{-1}$ . So according to this evidence, one can



Scheme

conclude that the two monohydroxy bridged copper (II) complexes are prepared.

## EXPERIMENTAL

### $[(phen)_2Cu(OH)Cu(phen)_2](Cl)_3 \cdot 3.5H_2O$

10 mmol  $CuCl_2 \cdot 2H_2O$  in 100 mL of acetone was added to 22 mmol 1,10-phenanthroline. After 3 hours stirring and addition of 4.8 mmol aqueous solution of NaOH, the titled compound precipitated. Analytical data calculated for  $C_{48}H_{40}Cu_2Cl_3O_{4.5}$ : C, 55.74; H, 3.90; N, 10.84; Cu, 12.28. Found: C, 55.9; H, 3.9; N, 10.7; Cu, 12.1.

### $[(4,4'-bipy)_2Cu(OH)Cu(4,4'-bipy)_2](ClO_4)_3 \cdot 5H_2O$

To a 10 mmol of  $Cu(ClO_4)_2 \cdot 6H_2O$  in 150 mL of water, 22 mmol of 4,4'-bipy in 150 mL of acetone was added. After five hours of stirring at room temperature 4.8 mmol NaOH, was added and two titled complex was precipitated. The product is soluble in hot water and has been recrystallized from hot water. Analytical data calculated for  $C_{48}H_{50}N_8Cu_2O_{18}Cl_3$ :

C, 45.06; H, 4.57; N, 8.75; Cu, 9.93. Found: C, 44.8; H, 4.1; N, 8.6; Cu, 9.7.

Room temperature magnetic moments were measured by the Gouy's method [31] using  $[\text{HgCo}-(\text{SCN})_4]$  as calibrant [32,33] and all data corrected for diamagnetism [34] and TIP (taken as  $120 \times 10^{-6}$  cgsu/mol of binuclear copper(II) complex). The IR spectra of compounds were recorded with a Perkin-Elmer 1330 spectrophotometer as KBr pellets. ESR spectra of powdered samples at room temperature were recorded on a Varian 4502 x-band spectrometer and visible spectra were recorded on a Cary 14 spectrophotometer.

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